CHEMICAL ENGINEERING TRANSACTIONS

VOL. 37, 2014

A publication of AIDIC
The Italian Association of Chemical Engineering
www.aidic.it/cet

Guest Editors: Eliseo Ranzi, Katharina Kohse- Höinghaus

ISBN 978-88-95608-28-0; ISSN 2283-9216

DOI: 10.3303/CET1437015

Effect of Feedstock Demineralization on Physico-Chemical Characteristics of Arundo Donax Derived Biochar

Paola Giudicianni*[a], Giuseppe Cardone[b], Antonio Cavaliere[b], RaffaeleRagucci[b]

[a]DICMAPI - Università degli Studi Federico II di Napoli - ITALY
[b]Istituto di Ricerche sulla Combustione - C.N.R. Napoli – ITALY
giudicianni@irc.cnr.it

Solid residue derived from thermochemical degradation of vegetal biomass, generally named biochar, is currently under study for its potential agronomic value as soil amender and fertilizer. Feedstock pre-treatments aiming to a partial demineralization of the biomass could promote the development of char porosity by inducing modifications of the chemical and physical characteristics of the feedstock. In the present paper three different methods of feedstock demineralization have been applied on Arundo donax samples. Steam assisted pyrolysis of raw and demineralized Arundo donax has been carried out in a proper experimental apparatus up to 873 K, at pressure $P=5\times10^5$ Pa and heating rate HR=5 K/min. A comparison of the chemical and physical properties of produced chars and energetic content of gaseous phase has been evaluated for its possible use as fuel to sustain biochar production itself.

1. Introduction

Pyrolysis represents an interesting process to recover matter from waste biomass and produce bio-oil and gas to sustain the process itself. An emerging use of solid residue is linked to the discovery of its agronomic and environmental value given its ability to enhance soil fertility through soil stabilization by aggregation, and retention of nutrients and water (Downie et al., 2009); at the same time, thanks to biochar recalcitrance, it contributes to mitigate climate change by long term carbon sequestration in soil (Lehmann et al., 2006). Moreover, the mineral ash content of biochar may have a liming and fertilizing effect when added to soil (Van Zwieten et al., 2010).
The feedstock material used for pyrolysis has a strong influence on the initial biochar characteristics (Gaskin et al., 2008). The vascular structure of the original plant material, for example, is likely to contribute for the occurrence of macropores in biochar identified as access routes to smaller pores. In contrast, micropores, mainly formed during processing of the parent material, effectively account for the large surface area in charcoals (Brown, 2009). As for the structural characteristics, also the chemical properties of biochar such as carbon content, char aromaticity and nutrients content are strictly dependent on feedstock characteristics. Previous studies (Raveendran et al., 1995) indicate that small amounts of inorganic material, as is present in the biomass, are sufficient to alter the pyrolysis behavior, and, consequently, both products distribution and properties to a large extent. Mineral matter promotes reactions of condensable species leading to the formation of compact secondary char. Moreover, it can prevent porosity evolution by blocking the access of activating agent to internal char porosity. Among the methods, proposed in literature, aimed to the removal of inorganic constituents, leaching treatments seems to be effective and easy-to-operate methods (Liu et al., 2011). Water leaching provides the removal of water-soluble inorganic elements, such as K, Na, Ca, Cl, S, and Mg. Besides, it is a low cost method having a low environmental impact given the possibility to dispose the leachate into the field or recovered by distillation or reverse osmosis techniques. Non water-soluble elements need dilute acid solutions (HCl, HF and HNO_3) to be removed. Nevertheless, acid leaching hydrolyses the hemicellulose and cellulose into smaller molecules that may impact on biomass and its products (Das et al., 2004). The large-scale application of acid washing method is, however, limited by the related not negligible environmental impact.

Please cite this article as: Giudicianni P., Cardone G., Cavaliere A., Ragucci R., 2014, Effect of feedstock demineralization on physico-chemical characteristics of arundo donax derived biochar, Chemical Engineering Transactions, 37, 85-90 DOI: 10.3303/CET1437015

In this study, Arundo donax as been studied as precursor of biochar and biogas through a steam assisted slow pyrolysis process. In order to improve biochar properties three different methods of feedstock demineralization differing for the chemical nature of the washing solution, temperature and duration of the treatment have applied on Arundo samples. A comparison of the characteristics of char and gas properties has been provided.

2. Experimental

2.1 Sample preparation and characterization

Arundo donax canes have been milled and the sieved fractions between 15 and 500 μm have been oven dried at 378 K to a constant weight before the demineralization treatments. Three demineralizing solution have been selected: distilled water, HCl 0.1 M and HCl 3.5, named in the following as H_2O HCl-01 and HCl-35. Six grams of each Arundo sample have been immersed in 120 mL of the three demineralizing solutions at 303 K with constant stirring. At the end of the treatment the solutions were filtered and washed with distilled water to a constant pH value, and the treated samples were dried at 378 K over 24 h. Feedstock has been characterized in terms of extractives, hemicellulose, cellulose and lignin content, presented in Table 1, according to the method described in Yang et al. (2006). Ash content has been evaluated by incineration in air at 600 °C for 2 h. The content of selected inorganic elements (Ca, K, Mg, Na and P), reported in Table 3, has been determined by Inductively Coupled Plasma Mass Spectrometry (ICP/MS). Elemental analysis of the biomass, shown in Table 2, has been performed using two different elemental analyzers (LECO CHN 2000 and LECO CS) for the determination of C, H, N and S. Nitrogen and sulphur has not been detected in all the samples and their content has not been reported in Table 2.

Table 1: Component analysis of untreated and demineralized Arundo donax (wt % dry basis)

	AC	AC-H_20	AC-HCl-01	AC-HCl-35
Extractives	6.5	6.7	6.0	4.4
Ashes	5.1	2.6	2.5	3.6
Hemicellulose	28.2	28.9	28.2	21.8
Cellulose	40.4	41.4	36.3	27.7
Lignin	19.7	20.2	27.0	42.5

Table 2: Chemical analysis of untreated and demineralized Arundo donax (dry sample basis)

	H (wt%)	C (wt%)	O (wt%)	H/C (mol/mol)	O/C (mol/mol)	Ca (mg/kg)	K (mg/kg)	Mg (mg/kg)	Na (mg/kg)	P (mg/kg)
AC	6.1	43.0	45.8	1.69	0.8	487	10620	245	108	663
AC-H_2O	6.2	44.6	46.4	1.65	0.78	426	161	114	6	46
AC-HCl-01	6.2	44.6	46.7	1.65	0.79	9	29	13	0	67
AC-HCl-35	6.3	45.5	44.6	1.65	0.74	10	16	18	4	2

As for component analysis, it should be noted that in both cases of acid pretreatment a reduction of the original amount of sample has been observed, respectively equal to 80 % and 56 % for HCl-01 and HCl-35 method, due to the hydrolyzation of holocellulosic fraction and a partial washing of extractives. As a consequence, the actual amount of lignin in both cases is not altered by the pretreatment, though its relative percentage increases. At the same time, the amount of ashes after each pretreatment is reduced, but the relative percentage after HCl pretreatments remains equal and even higher (e.g. HCl-35 pretreatment) than the one registered after water washing. The efficiency of demineralization method has been found to be varying for the different pretreatments and for the different inorganic species. H_2O method performs an efficient reduction of alkali metal ions (K and Na) and phosphorus, while acid solution is necessary for the removal of earth metal ions (Ca and Mg). The changes in sample composition induced by the pretreatment method do not affect H/C and O/C ratio.

2.2 Experimental apparatus and products analysis

In this steam pyrolysis of untreated and demineralized Arundo donax canes have been carried out in a pyrolysis reactor, whose details are given in Ragucci et al. (2013), at constant heating rate (HR_{sp}=5 K/min) and pressure (P= 5×10^5 Pa) up to final temperature T_f= 873 K. The test reactor consists of a prismatic chamber in which a 6 grams sample of biomass are spread in thin layers (approximately 1 mm thick) over 5 trays. Steam, heated to the programmed temperature, enters the reaction chamber at mass flow rate maintained at 0.25 g/s during the tests. Gaseous stream exiting the reaction unit passes through a condensation device where condensable species are collected, while non-condensing gases are sampled on-line. Products of steam pyrolysis test have been characterized as follow. Char yield has been determined as the weight loss of the original feedstock. The gas yield has been obtained by online monitoring of gas composition and carrier (N_2) flow rate, while liquid yield has been evaluated as the amount needed to complete the mass balance with respect to the feedstock sample. Chemical analysis of gas phase has been performed using a gas chromatograph equipped with a thermal conductivity detector (TCD) (Agilent 3000 Quad) attached directly to the sampling point allowing the simultaneous detection of all the species of interest (CO, CO_2, H_2, CH_4, C_2H_4, C_2H_6, N_2 and O_2). SEM analysis has been performed to study char morphology, while surface area (BET surface) has been evaluated by generating N_2 adsorption curves isotherms at 77 K (Autosorb-1, Quantachrome). Chemical composition of solid residue have been determined through elemental analysis (LECO HCN 2000) for the determination of H, C, N, and O content and with ICP/MS for the evaluation of selected inorganic species content (Ca, K, Mg, Na and P). The total content of ashes in the char has been measured by incineration in air at 600 °C for 2 h.

3. Results and discussion

In this section the results obtained from steam assisted pyrolysis experiments of Arundo canes have been presented and discussed in relation to the ones obtained from three types of demineralized canes. In order to evaluate a possible pretreatment capable to improve morphological and chemical characteristics of char, products yield have been determined and porosity, morphology and chemical composition of char have been evaluated. Moreover, the yield of gaseous species produced from pyrolysis of untreated and treated Arundo samples have been evaluated together with the corresponding High Calorific Value (HHV). In Figure 1a and b the yields of pyrolysis products respect to the sample fed to the reactor (Y_F) have been shown together with the yields of the same products scaled taking into account the weight loss of Arundo samples after the pretreatments (Y_P).

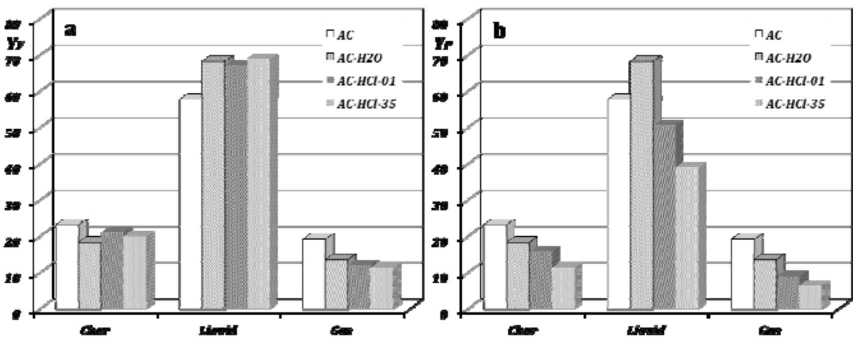

Figure 1: Effect of demineralization treatments on the yields of products from steam pyrolysis of Arundo donax

In Figure 2a and b gaseous species of untreated and demineralized Arundo canes have been reported. In agreement with previous literature (Raveendran, 1995), all the examined demineralization pretreatments induce modifications in pyrolysis behaviour of Arundo canes determining a reduction of char and gas yield in favour of an increase of liquid yield. At first glance, the different washing solutions used in the three pretreatment methods do not affect the yields of the pyrolysis products Y_F. In the case of water washing the removal of alkali metals favours the release of heavier condensable species from holocellulose fraction, while the release of lighter species and gas, mainly CO and CO_2 is depressed. In both cases of acidic washing solution two opposed driving force act on the determination of products yields. At increasing solution acidity, the increase of lignin content due to the hydrolyzation of holocellulose (see Table 1) enhances char production during pyrolysis. On the other hand, char yield decreases as a result of the enhanced devolatilization of heavier species due to the removal of alkali and earth metal ions. Overall, the tradeoff of these opposing effects results in comparable yields of products deriving from the pyrolysis of all the pretreated samples. Nevertheless, as results from Figure 1b, the different weight losses induced by the acidic washing solutions on the untreated sample determines a reduction of all the products yields evaluated on the basis of the untreated sample, progressively more pronounced with increasing solution acidity. As previously observed, pyrolysis of water washed Arundo samples produces lower yields of CO and CO_2 with respect to the untreated sample due to the removal of alkali ions. The reduction of the yields of CO_2 is more pronounced at increased acidity of sample pretreatment method not only for the additional removal of earth metal ions but also because of the reduction of holocellulose content. Monitoring CO releasing rate, not reported in this study for the lack of the room, the higher CO yield observed in the case of sample undergone to HCl-35 treatment is due to the enhancement of CO release at temperature typical of secondary decomposition of primary condensable species entrapped in the solid matrix. Given the comparable content of metal ions in both the samples treated with acid washing, it seems that the observed modifications on secondary decomposition pathways are due to the action of acid solution onto the organic matrix. A lower extent of secondary decomposition of condensable produced during primary pyrolysis is observed resulting in lower yield of CH_4 and C_2H_6 in all the treated samples. Among the treated samples, higher yield of CH4 are observed for the samples treated with both the acid solutions; this result could be explained with the increment of lignin content in acid pretreated sample due to acid induced hydrolization of holocellulose fraction. The decrease of H_2 yield in the water washed sample suggests that alkali metals have a catalytic role in char gasification reactions. In the samples undergone to acid washing the increase of the overall content of hemicellulose and lignin should promote H_2 production, given the main role of hemicellulose and lignin chars in gasification reactions with respect to cellulose char (Giudicianni et al., 2013). On the other hand, the lower content of alkali and earth metal ions depresses char gasific ation reactions. These two opposing driving forces result in a yield of H_2 comparable to the one obtained from water washed sample. Given the low final temperature investigated, Arundo donax canes undergone to thermal degradation produce low yield of gas made up mainly of CO_2 and CO that represent about 90 % in weight of the whole gas phase, while CH_4, H_2 and C_2 account for the remaining 10 wt%. Demineralization treatments determine modification in gas composition and consequently on the calorific value of the gas phase. HHV of gas deriving from untreated canes is about 7.3 MJ/kg. The H_2O treatment is responsible of a reduction of 13 % of HHV of the gas phase due to the higher content of CO_2. HHV increases progressively with the acidity of the washing solution and, in the case of HCl-35 treatment, it becomes even 13 % higher than the HHV of the gas from untreated sample thanks to the increase of CH_4 and CO content at the expense of CO_2 content. Nevertheless, considering the reduction of gas yields induced by the pretreatments the recovery in the gas phase of the energy content of biomass fed to the process is comparable for all the treated biomass, but always lower (about 35 %) than the one obtained from untreated Arundo canes.

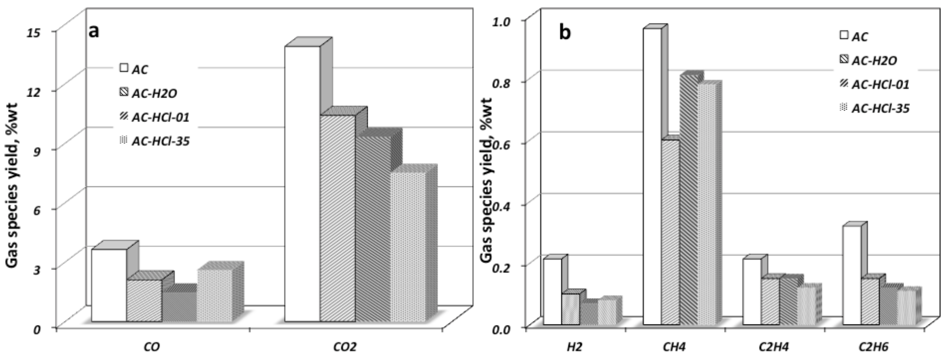

Figure 2: Effect of demineralization treatments on the yields of major (a) and minor (b) gaseous products from steam pyrolysis of Arundo donax

In view of the utilization of char as fertilizing agent for agricultural soils, the H/C and O/C ratio and nutrients content of char from untreated and treated canes has been evaluated. Specifically, H/C and O/C ratios indicate the degree of aromaticity and maturation of char, fundamental for the evaluation of char recalcitrance. The mild pyrolysis temperature applied to the biomass samples determines values of both H/C and O/C ratios quite higher than the ones typical of graphite-like structure, though char deriving from pyrolysis of HCl-35 treated sample is characterized by the lowest values of H/C and O/C probably because of the highest lignin content of the feedstock and to the enhanced devolatilization of oxygenated compounds. Untreated canes lose their nutrient content except for potassium that remains in concentration of about 200 mg/kg. Demineralization treatments remove almost completely the nutrient content of the corresponding char.
Morphological properties of char obtained from treated and untreated canes have been investigated through the evaluation of BET surface and adsorption isotherms, reported respectively in Figures 3 a and b. Scanning electron micrographs (SEM) of char from treated canes have been also carried out and compared to the ones obtained for char from untreated canes reported in a previous work (Giudicianni et

al., 2013). For the lack of the room only SEM micrographs of char from untreated and HCl-01 washed canes is shown in Figure 4. The abatement of inorganic species content determines a huge increase of BET surface. At the same way adsorption isotherms (N_2, 77 K) (Figure 4b) show that, even though for the char deriving from untreated canes the adsorption capacity is limited, an important development of char porosity is reached with all the pretreatment methods considered in this study. A typical vascular tissue of *Arundo donax* canes is made up of tracheids and vessels: the cell walls consist of cellulose fibers, immersed in an open matrix of hemicellulose and lignin. As it can be seen from Figure 4a, in the processed material the cellulosic fraction capable to develop a porous structure (Giudicianni et al., 2013) is completely embedded in a compact matrix of hemicellulose and lignin deriving from the recondensation of a plastic-like material. Moreover, it is worth noting that in the biomass cell walls present some perforations (pits) that allow the communication between the adjacent cells through a membrane made up of carbohydrates of middle lamella and primary wall.

Table 3: Elemental analysis of char from untreated and demineralized Arundo donax

	H (wt%)	C (wt%)	O (wt%)	H/C (mol/mol)	O/C (mol/mol)
AC	2.4	67.1	8.5	0.42	0.10
AC-H_2O	2.3	69.6	12.9	0.39	0.14
AC-HCl-01	2.2	77.1	8.8	0.34	0.09
AC-HCl-35	1.8	74.3	5.8	0.28	0.06

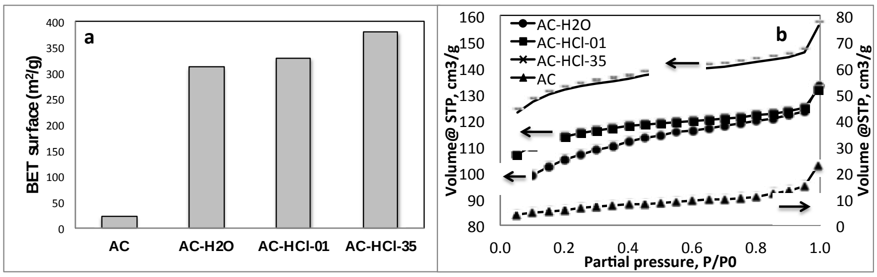

Figure 3: Effect of demineralization treatments on porosity of char from steam pyrolysis of Arundo donax

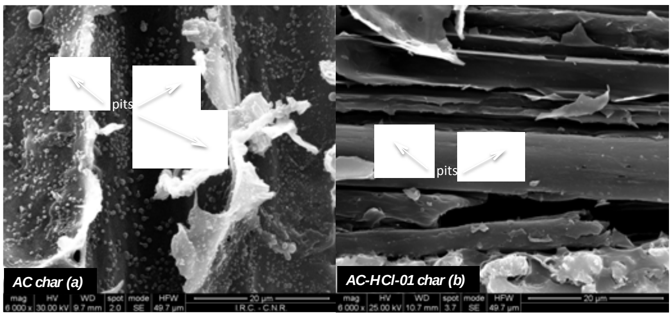

Figure 4: SEM micrographs of char obtained from AC and AC-HCl-01 samples at a magnification of 6000x

Charring of these membranes during steam pyrolysis could close the communication between adjacent cells preventing, in many cases, the access to cells internal porosity. Finally, it is well known that some inorganic species catalyze the production of secondary char characterized by a compact structure (Raveendran, 1995). Analysing adsorption isotherm of untreated Arundo char it is evident that the nitrogen uptake is concentrated in the low-pressure range, while in the high-pressure range, no further adsorption is observed and the adsorption curve reaches equilibrium except for a steep increase at the end of the curve. This isotherm is a Type I isotherm that represents microporous solids having a relatively small external surface area. In contrast char deriving from treated canes presents a more open structure probably due to the higher extent of volatile production during pyrolysis; moreover, char internal porosity is made accessible by open pits between vessels. This results in an enhancement of adsorption capacity of chars from treated canes. No substantial differences have been observed between H_2O and HCl.01

demineralization methods as for their effect on BET surface values, while HCl-35 treatment determines an additional increase of about 20 % of BET surface. At the same way, adsorption capacity of H_2O and HCl-01 chars is comparable and lower than the one measured for HCl-35 char. A more pronounced microporosity is observed for H_2O char while the continuous increase of adsorption with p/p_o in H_2O and HCl-35 char indicates the presence of a relevant mesopore fraction.

4. Conclusions

All the examined demineralization pretreatments induce modifications in pyrolysis behavior of Arundo canes determining a reduction of char and gas yield in favour of an increase of liquid yield due to an enhanced devolatilization. As for products yields, no remarkable differences have been observed between the different demineralization pretreatments. Nevertheless, the different weight losses induced by the acidic washing solutions on the untreated sample determines a reduction of all the products yields evaluated on the basis of the untreated sample.
Chemical and morphological nature of char is altered by pretreatments. Specifically char from HCl-35 treated sample is characterized by the lowest values of H/C and O/C indicating a higher recalcitrance of the solid residue. Moreover, the removal of inorganic species determines an increase of BET surface of one order of magnitude with respect to the one obtained for the char from untreated canes. The highest BET surface is obtained for char from HCl-35 treated sample. All demineralization treatments enhance microporosity of residual char, while the development of a mesoporous fraction is observed in the char derived from H2O and HCl-35 treated samples. These observations allow to conclude that the investigated pretreatments allow to obtain a more recalcitrant carbon based soil conditioner capable to improve only soil physical properties given its reduced nutrient content.
Finally, in view of the utilization of gaseous products to sustain energy required for biochar production, though the gas from the sample treated with HCl-35 has characterized by a higher HHV, considering the reduction of gas yields induced by the pretreatments, the recovery in the gas phase of energetic content of biomass fed to the process is comparable for all the treated canes and always lower than the one obtained for untreated Arundo canes.

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