

Do the Interactions between Biomass Organic Components and Alkali Metal Ions Affect Pyrolysis Liquid Composition? A Case Study on *Arundo Donax*.

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Abstract

Chemical characterization of pyrolysis liquids is fundamental in order to investigate their reactivity in view of the exploitation of their energetic content as well as for their suppression when they represent an undesired product in biomass gasification processes. In this paper the influence of feedstock composition (organic and inorganic matrix) on the products yields and the liquid phase composition deriving from a slow steam assisted pyrolysis process was studied. To this aim slow steam assisted pyrolysis tests at 5 K/min and final temperature equal to 973 K were carried out on cellulose (pure and doped with Na and K ions), on a biomass model mixture of cellulose, xylan and lignin alkali (Mix XCL) and on *Arundo donax* canes, untreated, demineralized.

Introduction

Chemical characterization of pyrolysis derived liquids is fundamental to investigate their reactivity not only in view of the exploitation of their energetic content but also for their suppression when they represent an undesired product in biomass gasification processes.

Yields and composition of pyrolysis liquids from wood and agricultural residues have been evaluated in different experimental configurations and operating conditions and reviewed in [1]. Findings of previous studies show the complexity of pyrolysis liquids composition characterized by the presence of water, oxygenated volatile compounds, polar not volatile species and high molecular weight compounds [1]. These studies put in evidence the relevance of biomass chemical composition in determining liquid product composition. It cannot be predicted simply on the basis of the separate thermal behavior of the three main biomass components (cellulose, lignin, hemicellulose), due to the occurring of significant mutual interactions during their thermal decomposition processes when they are closely interconnected as in a lignocellulosic matrix [2-6].

The presence of alkali and alkali earth metals absorbed on cellulose samples is known to affect the temperature and the mechanism of thermal decomposition during pyrolysis. These metals cause fragmentation of the monomers of cellulose, rather than their depolymerization determining the production of lighter volatiles in place of levoglucosan (1,6-anhydro- α -D-glucopyranose) [7, 8]. Inorganic salts, especially alkali earth metal chlorides, strongly enhance the formation of 2-furaldehyde from xylan pyrolysis [9]. As for lignin derivatives, yield of C6 lignin derivatives including phenol, guaiacol and syringol gradually increase in proportion to K ions content [10]. The effect

of alkali metals observed for cellulose has been recognized also in the case of real biomasses [11-13].

In this work a systematic approach was used to investigate the effect of possible interactions between biomass components and inorganic ions (Na and K) typically present in real biomasses on pyrolysis liquids composition and on the onset of gasification reactions. To this aim pure and doped (with K and Na ions) cellulose samples have been compared to investigate the effect of alkali species. Than the results obtained from a real mixture of xylan, cellulose and lignin, resembling *Arundo donax* composition, have been compared with the results calculated from the superposition of the data obtained from single components in order to highlight possible interactions. Finally, results obtained from pure, washed and Na doped *Arundo donax* have been compared to those of the biomass model mixture.

Materials and methods

Beechwood xylan, cellulose fibers and lignin alkali (X4252, C6663, 370959 from Sigma Aldrich, respectively) have been used as representative models of biomass components. *Arundo donax*, harvested in San Giorgio del Sannio (Italy), has been used as real biomass. The samples used for the pyrolysis tests have been listed in Table 1. The chemical characterization of the feedstocks used for the samples preparation is reported in Giudicianni et al. [14]. It is worth to be noted that xylan and lignin have a not negligible content of Ca, K and Na ions whose presence is possibly due to the alkali-based extractive procedure. The presence of such ions has to be taken into account as possible factor influencing the pyrolysis behavior of the real model mixture.

The model mixture of xylan, cellulose and lignin (Mix XCL) has been prepared in such a way that the amount of the pure component in the mixture was equal to the amount of the corresponding pure component in the *Arundo donax* sample.

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Sodium and potassium added cellulose, C_{Na} and C_K , have been prepared according to the procedure reported by Patwardhan et al. [8]. The salt concentration in the sample has been fixed at 0.1 mmol/g_{cellulose} since, in the case of cellulose pyrolysis, this is the minimum concentration that provides the higher effect in terms of catalytic effect on pyrolysis liquids [8].

Arundo donax canes have been milled in a mixer and sieved in the 400-600 μ m size range to ensure homogeneous feeding of the reactor. A mild *Arundo donax* canes demineralization procedure has been preferred with respect to the typical diluted acid treatment (HCl, HF and HNO₃) [15] with the aim to achieve high minerals removal efficiency without altering the amount and the chemical nature of holocellulose in the original biomass (i.e. hydrolyzation of hemicellulose and cellulose into smaller water-soluble molecules). ICP/MS analysis performed on washed sample shows an high removal efficiency for phosphorus and alkali metals (70-93%), while the removal efficiency is lower (38-54%) for alkaline earth metallic species [14]. Steam pyrolysis experiments have been carried out at constant heating rate ($HR_{sp}=4$ K/min) and pressure ($P=5\times 10^5$ Pa) up to final temperature $T_f=973$ K in a pyrolysis reactor described in details in Ragucci et al. [16]. Gaseous stream exiting the reaction unit passes through a condensation device and a flask submerged in a thermostatic bath at 273 K collects the condensed volatiles for subsequent off-line chemical characterization. The pyrolysis liquids have been extracted with dichloromethane (DCM). The resulting non polar fractions have been injected in a Gas Chromatogram/Mass Spectrometer (GC/MS) HP6890/HP5975 for qualitative analysis. The gas chromatograph is equipped with an Agilent HP-5MS capillary column. Helium has been used as carrier gas with a constant flow of 1.0 mL/min. The oven temperature has been programmed at 313 K and held for 3 min, than it has been raised to 573 K at a heating rate of 5 K/min and held at 573 K for 20 min. The mass spectrometer has been operated in electron ionization mode, and a m/z range from 30 to 400 Da/e has been scanned.

The amount of levoglucosan in each sample has been evaluated by Gel Permeation Chromatography (GPC) by using a 12 μ m TOSOH TSK G3000 PWXL gel column on a Agilent 1260 HPLC system equipped with a UV-DAD and a RID detectors. For each run 100 μ L of sample have been injected, and the elution has been monitored by reading the variation of the refractive index. The chromatographic analyses have been performed in isocratic conditions by using water as eluent and a flow rate of 0.5 mL/min. The separation and the identification of the other pyrolysis products have been achieved by chromatographic analyses on a 5 μ m SUPELCO RP-C18 column. For each run 100 μ L of a 1:10 diluted sample have been injected. The elution has been monitored by reading the UV absorption at 210 nm and 280 nm depending on the considered species. The chromatographic analyses have been performed at a

flow rate of 0.8 mL/min by applying a linear gradient of methanol: from 0 to 100% of methanol in 30 minutes followed by 5 minutes in isocratic conditions with 100% water.

Abbreviation	Description
C	Cellulose
C_{Na}	NaCl doped cellulose
C_K	KCl doped cellulose
X	Xylan
L	Lignin
Mix XCL	Mixture of xylan, cellulose and lignin resembling <i>Arundo donax</i> canes composition
Mix (XCL) _c	Calculated mixture of xylan, cellulose and lignin resembling <i>Arundo donax</i> canes composition
Mix (XC _{Na} L) _c	Calculated mixture of xylan, NaCl doped cellulose and lignin resembling <i>Arundo donax</i> canes composition
Mix (XC _K L) _c	Calculated mixture of xylan, KCl doped cellulose and lignin resembling <i>Arundo donax</i> canes composition
AC	Untreated <i>Arundo donax</i> canes
DAC	Demineralized <i>Arundo donax</i> canes

Tab. 1 List of the abbreviations.

Results and discussion

The results obtained from C, C_{Na} , and C_K have been compared to investigate the effect of typical alkali species present in biomass. Then the experimental results obtained from Mix XCL have been compared with the results computed for the three mixtures, Mix (XCL)_c, Mix (XC_{Na}L)_c, Mix (XC_KL)_c in order to highlight possible interactions between biomass components and to attempt identifying the effect of massive presence of alkali metals in commercial xylan and lignin. Finally, the results obtained from AC and DAC have been compared to verify the findings achieved on the biomass model mixture.

Qualitative information about the composition of pyrolysis liquids has been achieved by GC/MS analysis. Only information about the non-polar fractions (extracted in DCM) has been obtained due to the intrinsic limitation of the GC/MS approach. The total ion current (TIC) chromatograms of the DCM extracts of the pyrolysis liquids are not reported for space constrains. They show that the pyrolysis liquid from cellulose, as expected, mainly contains furan derivatives such as furfural (2-furancarboxaldehyde), furfurylic alcohol (2-furanmethanol), 5-methyl furfural (5-methyl-2-furancarboxaldehyde) and 5-hydroxy methyl furfural (HMF). The DCM extract of pyrolysis liquid from xylan is mainly composed by furan derivatives as furfural and furfurylic alcohol, as found for cellulose. As expected on

the basis of xylan structure, where only a few number of hexoses units is present, HMF has not been detected because under the instrument detection limits. The DCM extract of pyrolysis liquid from lignin is mainly composed by oxygenated aromatic compounds, such as phenols, benzenediols (catechols), and phenols with methoxysubstitutes (guaiacols, syringols, and vanillin derivatives). The species detected for doped cellulose sample are the same as those found for pure cellulose, but the relative abundances are different.

The DCM extract of Mix XCL is, as expected, a mixture of the species identified for the single components. It is noteworthy the higher relative abundance of furfuryl alcohol (11.2 %) with respect to that of furfural (2.17 %) and the absence of HMF consistently with the presence of inorganic salts.

A result analogous to the cellulose sample doped with Na ions has been observed for the liquid obtained from the pyrolysis of *Arundo donax* canes. The relative abundance of furfuryl alcohol is higher with respect to that of furfural and the HMF is not detectable in the untreated biomass while in the demineralized sample furfural and furfuryl alcohol exhibited a quite comparable relative abundance. The HMF relative abundance in this case is not negligible (1.68%). In all the investigated cases the relative abundances of lignin derivate species are not affected by the presence of inorganic salts.

The information obtained by GC/MS analyses has been used to select the most relevant non-polar compounds as representatives of each biomass component (cellulose, lignin, xylan) to be quantified in the pyrolysis liquids. The species representative of the cellulose pyrolysis liquid are: levoglucosan, furfural, furfurylic alcohol and HMF. In the case of xylan are: anhydrosugars (derived from dehydration of xylose), furfural and furfurylic alcohol. Finally, for lignin are: phenol, catechol, guaiacol, syringol, p-cresol (p-methyl guaiacol) and p-ethyl guaiacol.

As it is evident in Figure 1, levoglucosan, as expected, is the most abundant molecule in the cellulose pyrolysis liquid (4.74 wt %) and its yield is comparable with literature data (around 6%) obtained from slow pyrolysis experiments in inert atmosphere [17]. Differently, when steam is used instead of nitrogen, furfural and HMF are produced in a larger amount. The yields of furfural and HMF are comparable (3.31 wt % and 3.19 wt %, respectively), while the yield of furfurylic alcohol is very low (about 0.01 wt %). As found for slow pyrolysis in inert atmosphere, also in the presence of steam, levoglucosan is the main product of cellulose depolymerisation through transglycosilation. The production of furfural and HMF through ring opening and rearrangement reactions of cellulose units or through levoglucosan secondary reactions, [18] seems to be enhanced in presence of steam.

Looking at the data for doped cellulose samples it is clear that the yields of species selected for cellulose pyrolysis liquid characterization are largely affected by the presence of inorganic salts (Fig. 1). In particular,

when a small amount of NaCl ($< 0.1 \text{ mmol/g}_{\text{cellulose}}$) is present, the yields of levoglucosan, furfural and HMF dramatically decrease, and the furfurylic alcohol yield grows. These data are in agreement with those reported by Patwardhan et al. [8] and suggested that the Na ions, also in steam assisted conditions, could favour the ring-opening reactions of cellulose unit molecules at the expense of levoglucosan formation reaction. The effect of K ions is not so evident as that of Na ions. Looking at the Fig. 1, the furfural represents the most abundant (0.3 wt. %) furan detectable in the xylan pyrolysis liquid. Its yield is higher than that estimated for furfuryl alcohol (0.06 wt.%). Anhydrosugars, derived from dehydration of xylose, are also produced during xylan pyrolysis [9], but the absence of commercially available standards does not allow univocal identification. In our case, a signal in the SEC chromatogram due to anhydrosugars accounting for ca 3.5 wt. % has been identified and its quantification has been performed by using levoglucosan as standard being the levoglucosan structure similar to that of xylose dehydration products. These xylan derivatives have been quantified only for pure xylan since in the case of the ternary mixture and *Arundo donax* samples the xylose dehydration products signals are superimposed to other unknown signals. The RP-HPLC chromatogram of the xylan-derived pyrolysis liquid is characterized by many peaks of very low intensity whereas only furfural and furfuryl alcohol are univocally identifiable and quantifiable. This finding is in agreement with the GC/MS analysis in which only the 30% of the peaks are univocally identified. It is well assessed in literature that xylan pyrolysis vapours at high temperature underwent significant secondary cracking and gave high yields of gas products [19]. The enhanced cracking of the xylan pyrolysis vapours could also be ascribed to the presence in the commercial xylan sample used in this study of a high ash content, which is known to promote gas formation [13]. In the lignin-derived pyrolysis liquid, only monomeric phenolic compounds (phenol, catechol, guaiacol, syringol, p-cresol (p-methyl guaiacol) and p-ethyl guaiacol) have been identified and quantified. A water insoluble dark orange fraction, often indicated as pyrolytic lignin, has been detected on the bottom of the flask, and ascribed to more complex phenolic structures. Guaiacol represented the most abundant molecule in the lignin pyrolysis liquid (2.63 wt %), while syringol exhibited a low abundance (0.12 wt %). The yields of the other molecules are 0.60 wt % for catechol, 0.18 wt % for p-cresol, 0.24 wt % for phenol and 0.05 wt. % for p-ethyl guaiacol. The presence of these phenolic species is in agreement with the pyrolysis pathways proposed for thermal decomposition of lignin [19]. Such studies reported that the thermal decomposition of lignin lead to the release of guaiacyl- and syringyl-type aromatics derivatives (depending on the lignin source) through the cleavage of the weaker bonds, namely the ether ones. These aromatic derivatives could further decompose producing monomeric phenolic compounds [20].

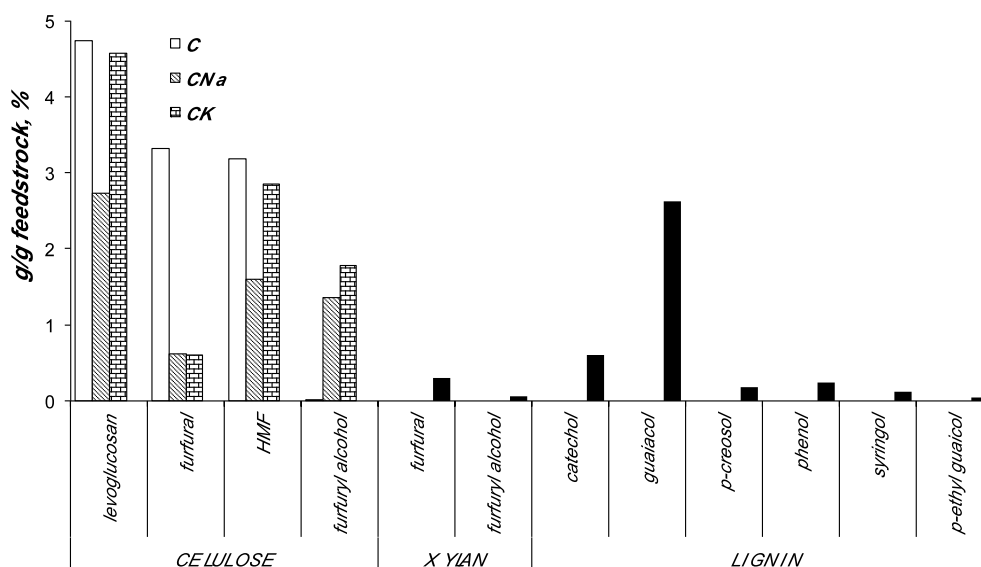


Fig. 1. Product distribution in the pyrolysis liquid from cellulose, xylan and lignin.

In Fig. 2 the experimental results on ternary mixture have been compared with those calculated on the basis of the experimental results from the pyrolysis of the single biomass components. The yields are calculated assuming that the ternary mixture pyrolysis behaviour is the weighted sum of the partial contributions of its components. The calculations have been performed by considering the data on pure cellulose as well as those on salt doped cellulose samples.

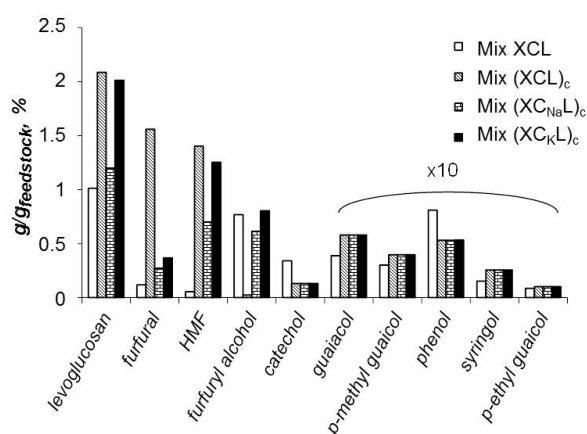


Fig. 2. Products distribution in the pyrolysis liquid from Mix XCL compared to the calculated ones Mix (XCL)_c, Mix (XC_{Na}L)_c, Mix (XC_KL)_c.

There are significant differences between the experimental and calculated compositions of the ternary mixture derived pyrolysis liquid. In particular, differently from the predicted data (Fig. 2, Mix (XCL)_c), in the real pyrolysis liquid (Mix XCL) there is a lower amount of levoglucosan, furfural and HMF and a negligible amount of furfuryl alcohol. The yields of the

species belonging to the decomposition of lignin fraction agree quite well with those calculated (Fig. 2, Mix (XCL)_c). This last finding agrees with literature data and it confirms the negligible effect of inorganics on the pyrolysis behaviour of lignin fraction [21]. A better prediction has been obtained in the case of calculation performed by considering the data on salt doped cellulose samples (Fig. 2, Mix (XC_{Na}L)_c, (Mix (XC_KL)_c). Looking at the data in Fig. 2, it is clear that when the three biomass components are mixed together, the cellulose and xylan product distribution, differently from that of lignin, is largely affected by the presence of salt contamination and/or by the development of interactions among components. However the comparison with the calculated data and the literature data [8,9] indicates that the presence of salt contamination (Na and K ions) is the principal driving force leading to lower yields of derivatives (mainly levoglucosan, HMF, furfural) through a catalytic effect on primary cellulose and xylan pyrolysis reactions. On the basis of the differences observed between the experimental and the calculated results it is evident that the prediction of the chemical composition of the pyrolysis liquid is even more challenging than the prediction of the pyrolysis products yields.

The product distribution in the pyrolysis liquids from the three *Arundo donax* samples is reported in Fig. 3. It exhibits differences ascribable to the presence of inorganics.

As expected, the yields of cellulose and xylan derivatives are lower for the raw *Arundo donax* sample (AC) with respect to those estimated for the demineralized sample (DAC). In particular, in the case of DAC, the yield of levoglucosan (2.88 wt. %) is three times higher than those estimated for the raw sample

(0.95 wt.%) while the furfural and HMF yields are almost twice (0.41 wt. %) and four times (0.28 wt. %) than those estimated for the raw sample (0.23 and 0.07 wt. %, respectively). Only the furfuryl alcohol yield is lower (0.54 wt. %) than the raw sample (0.73 wt. %).

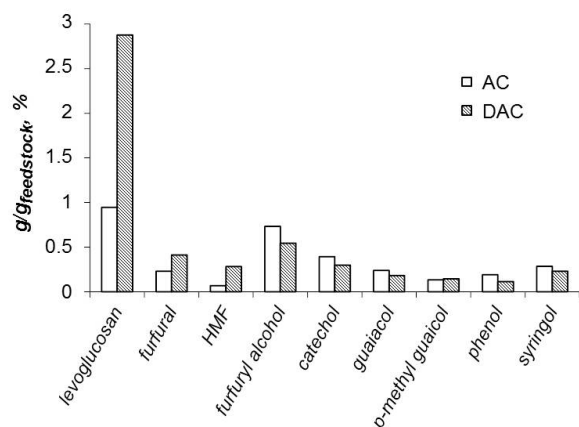


Fig. 3. Products distribution in the pyrolysis liquid from the three *Arundo donax* samples.

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Conclusions

The results obtained in the present study allow to conclude that the addition of alkali metal ions affect cellulose pyrolysis. The yields of levoglucosan (the most abundant molecule in the cellulose pyrolysis liquid) and furans decrease when Na ions are added. In particular the presence of Na ions favours the formation of furfuryl alcohol at the expense of furfural and HMF. The effect of K ions is not so evident as that of Na ions. In all the investigated cases the relative abundances of lignin derivate species are not affected by the presence of inorganic salts.

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