



# Influence of possible interactions between biomass organic components and alkali metal ions on steam assisted pyrolysis: A case study on *Arundo donax*



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## ABSTRACT

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 and on *Arundo donax* canes, untreated and demineralized. Products yields were measured. Chromatographic techniques were applied to identify and quantify the main species in the gaseous and in the liquid fractions. This study showed that alkali metal ions affected both the devolatilization and gasification stages. More specifically, their presence depressed the levoglucosan yield due to cellulose decomposition and enhanced the production of CO<sub>2</sub> and H<sub>2</sub> in the gasification stage.

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## 1. Introduction

Slow pyrolysis represents a way to produce a solid material, named char, with improved characteristics with respect to the original biomass [1,2]. In this case, pyrolysis liquids could represent a by-product that can be used to assist energetically the pyrolysis process [3]. On the contrary, pyrolysis liquids represent an undesired product in biomass gasification processes [4], mainly in updraft and downdraft gasifiers, where they are produced in the operating conditions typical of conventional pyrolysis also in presence of steam. 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. Moreover, the comprehension of the involved interactions between organic and inorganic components of the biomass is a relevant issue since demineralization pretreatments of agricultural residues are commonly used as a preliminary step before thermochemical conversion processes [2–5]. The dependence of liquid chemical composition on the feedstock chemical characteristics is still to be clarified. Studies concerning the influence of interactions between biomass components during primary and secondary pyrolysis show that liquid product composition 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. Hosoya et al. [6,7] found that although cellulose–hemicellulose interactions are negligible, considerable effects on the pyrolysis behavior including liquid composition have to be considered between cellulose and lignin.

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Different results have been obtained by other authors [8–10], which concluded that limiting or enhancing mechanisms due the contemporary presence of cellulose, hemicellulose and lignin affect liquid composition. It is worth to be noted that in most of these studies [8–10] the presence of inorganic species in model compounds used to simulate biomass components has been neglected generating incomplete results.

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- $\alpha$ -D-glucopyranose) [11,12]. Inorganic salts, especially alkali earth metal chlorides, strongly enhance the formation of 2-furaldehyde from xylan pyrolysis [13]. As for lignin derivatives, yield of C6 lignin derivatives including phenol, guaiacol and syringol gradually increase in proportion to K ions content [14]. The effect of alkali metals observed for cellulose has been recognized also in the case of real biomasses [15–18].

The differences in the experimental conditions and substrates do not allow a quantitative comparison among the findings of the various studies concerning the influence of organic components interactions and inorganic species on pyrolysis liquids. Moreover, only in few cases [9,19,20] the presence of an oxidizing agent (steam) has been considered.

Present work stems from previous studies [21,22] on steam assisted pyrolysis of binary and ternary mixtures of biomass components. 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 *A. donax* canes have been compared to those of the biomass model mixture.

## 2. Materials and methods

### 2.1. Feedstocks and sample preparation

Beechwood xylan, cellulose fibers and lignin alkali (X4252, C6663, 370959 from Sigma–Aldrich, respectively) have been used as representative models of biomass components. Xylan has been chosen because it is the most representative component of hemicellulose. Lignin alkali has been chosen due to the robustness of the knowledge on its behavior in a wide variety of pyrolysis conditions [23–26]. *A. donax*, harvested in San Giorgio del Sannio (Italy), has been used as real biomass. Only canes and not leaves or mix of both have been used in this work, since canes composition resembles the average composition of most biomasses in terms of hemicellulose, cellulose and lignin content [27]. All the chemicals and the solvents used in this study have been purchased from Sigma–Aldrich. 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. [22] and in Supporting information (SI) (Tables S1 and S2). It is worth to be noted that xylan and lignin have not a 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.

In the case of single component pyrolysis tests, cellulose, xylan and lignin have been used to feed the reactor without any preliminary treatment except for a moisture removal procedure in an oven at 378 K. The same drying pre-treatment has been made for all the feedstock.

The other samples have been prepared as described in the followings. 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 *A. donax* sample. More details are reported in Supporting information (Table S3).

Sodium and potassium doped cellulose samples, C<sub>Na</sub> and C<sub>K</sub>, have been prepared according to the procedure reported by Patwardhan et al. [12]. The salt concentration in the sample has been fixed at 0.1 mmol/g<sub>cellulose</sub> 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 [12]. The appropriate amount of NaCl and KCl (37 mg and 45 mg, respectively) has been dissolved in 25 mL of deionized water and added to 6 g of cellulose. The suspension has been stirred for 30 min to obtain a well-mixed slurry and dried in an oven at 378 K.

*A. donax* canes have been milled in a mixer and sieved in the 400–600  $\mu$ m size range to ensure homogeneous feeding of the reactor.

A mild *A. donax* canes demineralization procedure has been preferred with respect to the typical diluted acid treatment (HCl, HF and HNO<sub>3</sub>) [28] 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). *A. donax* canes used in our tests contain mainly phosphorus, alkali and alkaline earth metallic species (see SI, Table S2). Component analysis of washed canes confirms that the leaching procedure has not altered the amount of holocellulose with respect to the untreated canes (see SI, Table S1). 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 (see SI, Table S2).

The demineralized *A. donax* canes have been used also to prepare a NaCl doped sample. The salt concentration (0.1 mmol/g) and the preparation procedure are the same applied for doped cellulose samples.

### 2.2. TGA analysis

Thermogravimetric analyses (TGA) have been performed on a PerkinElmer Pyris 1 thermogravimetric analyzer by heating the sample (2–10 mg) at atmospheric pressure in inert environment (N<sub>2</sub>, 40 mL/min) from 323 K up to 973 K with a heating rate (HR) of 4 K/min.

### 2.3. Pyrolysis tests

Steam pyrolysis experiments have been carried out at constant heating rate (HR<sub>sp</sub> = 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. [29] and reported in Supporting information (Fig. S1). It consists of a jacketed prismatic chamber in which 6 g of biomass are spread in thin layers (approximately 1 mm thick) over 5 trays along the rectangular cross-section of the inner reaction chamber. A steam generator produces steam that is heated to the programmed temperature in a super heater, and then, enters the reaction chamber, passing through a flow straightener, at mass flow rate corresponding to an average residence time of the gas phase in the reactor ranging from 1.5 to 3 s in dependence on the reactor temperature. Gaseous stream exit-

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