



Full Length Article

Effect of alkali metal ions presence on the products of xylan steam assisted slow pyrolysis

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ABSTRACT

Biomass pyrolysis has been extensively investigated during the last decades both as a stand-alone process for the production of bio-based fuels and as intermediate stage in other thermochemical processes such as gasification and combustion. The comprehension of biomass pyrolysis mechanisms can greatly benefit from the study of the pyrolysis behavior of separated biomass organic components as well as of the effect of metal ions on their decomposition pathways. Only few works reported the metal ions effect on the pyrolysis of hemicellulose. In the present paper the influence of metal ions on hemicellulose pyrolysis was studied choosing commercial xylan as reference. The thermal behavior of raw and demineralized xylan samples was studied in a thermogravimetric apparatus at atmospheric pressure under nitrogen from 323 K up to 973 K with a heating rate of 5 K/min. Then steam assisted pyrolysis tests were carried out up to two different final temperatures, 873 and 973 K, at pressure $P = 5 \times 10^5$ Pa and heating rate $HR = 5$ K/min. Products yields, gas releasing rates as a function of the temperature, gas and liquid compositions were compared for raw and demineralized samples. The raw and demineralized xylan exhibited different pyrolytic behaviors both in nitrogen and steam atmospheres. Raw xylan produced a higher amount of char compared to the demineralized one in nitrogen atmosphere, whereas negligible differences in char yields were observed in presence of steam. Demineralization pretreatment resulted in the recovery of a greater amount of furfural and depressed the production of gas in both the pyrolysis and the gasification stages.

1. Introduction

Interest in creating bio-based energy and materials supply chains has grown over the last few decades. Thanks to its high flexibility with respect to the desired product – bio-oil, bio-gas or char [1] – pyrolysis of biomass can be considered as a route to the production of both smart energy carriers and a valuable material, the biochar, from waste residues [2,3]. Steam assisted slow pyrolysis conditions at temperatures lower enough to prevent excessive char consumption (< 873 K) allow to combine the production of high quality char and a vapor phase that could be used to assist energetically the process [4]. Biomass chemical composition affects greatly both products yield and characteristics given the different chemical nature and distribution of its main organic components, namely cellulose, hemicellulose and lignin. The interactions between the organic components affect products yield and characteristics [5–11]. Moreover, inherent alkali and alkaline earth metallic (AAEM) species are known to affect the temperature and the mechanism of biomass thermal decomposition during pyrolysis. A wide literature is available on the effect of AAEMs on pyrolysis of biomass

and single biomass components [5,12–29]. It has been proven that K, Na, Ca and Mg affect at a different extent the primary decomposition of the organic constituents of the biomass, promoting char formation and secondary reactions both in slow and fast pyrolysis conditions and whatever feedstocks are used, individual constituent or biomass samples.

More specifically, in the case of cellulose the presence of AAEMs was found to depress the production of levoglucosan in favor of lower molecular weight species (especially formic acid, glycolaldehyde and acetol) both in slow and fast pyrolysis conditions. Moreover, slow pyrolysis experiments showed that alkali and even more earth alkali metals reduced the initial temperature of cellulose decomposition [5,22].

Only few works reported about the effect of metals on hemicellulose and lignin pyrolysis [25–27].

The catalytic effect of alkali and alkaline earth metals on hemicellulose fast pyrolysis has been studied and, in agreement with what observed for cellulose, they promote the ring-scission (formation of non-condensable gases and light oxygenates) and dehydration reactions

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(formation of 2-furaldehyde and char) in competition with the depolymerization, water addition (formation of anhydro xylose and xylose), and single dehydration reactions (formation of dianhydro xyloses) [25].

When impregnated in lignin, AAEMs had no significant effect on pyrolysis products [26,27] except for a higher conversion of methoxy groups to methanol [30,31].

Even if AAEMs cause small variations of the energy potential of the vapor phase, they greatly affect its chemical composition and, consequently, its combustion characteristics in real combustion systems [32]. Moreover, when vapor phase is condensed and stored the presence of alkali metals reduces its stability [14,29]. It is clear that the removal of inherent inorganics by water leaching pretreatments could be useful to tailor the characteristics of both char and vapor phase. This is even truer if one considers that in the thermal conversion of solid fuels, and particularly of biomass, the hot flue gas is usually contaminated with alkali species (Na, K), also in form of fly ashes, causing plant clogging due to their low melting points and high reactivity [33]. The role of inorganics on biomass components pyrolysis is not completely understood and deserves further experimental studies.

Hemicelluloses constitute about 20–30% of the total mass of annual and perennial plants and have a heterogeneous composition, containing various sugar units. Depending on the type of plant and extraction process, hemicelluloses are classified as: xylans (β -1,4-linked D-xylose units), mannans (β -1,4-linked D-mannose units), arabinans (β -1,5-linked L-arabinose units), and galactans (β -1,3-linked D-galactose units) [34]. Xylans are the main hemicelluloses in hardwood. Xylan general structure consists in a linear backbone of 1,4-linked D-xylopyranose residues with a furanose reducing sugar. This polysaccharidic backbone may be substituted with groups as acetyl, arabinosyl, and glucuronosyl residues, depending on the botanic source and method of extraction [34]. Hemicelluloses isolation techniques result in a significant amount of mineral residues in the extracted hemicellulose, and also in some structural modification, as for example the removal of acetyl groups [35]. The complexity, the less defined structure, and the unsatisfactory isolation techniques explain the very limited information about hemicellulose pyrolysis. Commercially available xylan has often been used as representative for hemicellulose in pyrolysis experiments, but often it has an extremely high content of AAEM (for example the xylan supplied by Sigma-Aldrich) making its complete demineralization quite challenging.

In this work we performed a quite complete demineralization of commercial beechwood xylan and we compared its pyrolysis behavior with the raw xylan in order to acquire data aimed to understand more about the effect of alkali and earth alkali metals on xylan pyrolysis. The thermal behavior of raw and demineralized xylan samples was studied in a thermogravimetric (TG) apparatus up to 973 K with a heating rate of 5 K/min under N_2 at atmospheric pressure. Then steam assisted pyrolysis tests were carried out up to two different final temperatures, 873 and 973 K, at pressure $P = 5 \times 10^5$ Pa and heating rate $HR = 5$ K/min. The choice of the experimental conditions and the motivation of design criteria of the experimental apparatus has been presented and discussed in [36]. Previous studies on cellulose pyrolysis, whose results are summarized in [36], have demonstrated that an increase in pressure, generally linked to higher gas residence time in the reaction environment, generates higher char yields and produces lighter volatiles. A previous study conducted in the same experimental apparatus used in the present work demonstrates that in our operating conditions at $T = 873$ and 973 K char yield is negligibly affected by the increase of pressure up to 5×10^5 Pa and the secondary reactions are only slightly affected in favor of gas production by an increase of the pressure due to the low gas residence time. Since in the operating conditions selected for this study the pyrolysis process is not very sensitive to the pressure, at least in the range $1\text{--}5 \times 10^5$ Pa, it has been decided to operate at elevated pressure because the operating conditions of the experimental plant are more easily controllable and stable and this is an important requirement when different sets of experimental tests need to be

compared. In this work products yields, gas releasing rates as a function of the temperature, gas and liquid compositions were compared with the aim to increase the comprehension of hemicellulose pyrolysis behavior and to pave the way for the formulation of possible decomposition mechanisms.

2. Experimental

2.1. Materials

All the chemicals and the solvents used in this study were purchased from Sigma–Aldrich and, except for xylan, they were used without any further purification. Beechwood xylan was purchased from Sigma–Aldrich (X4252) and used as representative model of hemicelluloses.

The raw xylan was demineralized by using a cation-exchange resin (Dowex® 50WX8; H^+ form, 100–200 mesh, 2,17,506 from Sigma Aldrich). The cation-free polysaccharide was obtained as follows: 7 g of raw xylan were dissolved in 200 mL of water and passed through 20 mL of cation-exchange resin (the resin before the use was washed with water in order to remove any contaminants), the resulting eluate (pH around 2.5) was then freeze-dried and the demineralized xylan was recovered as a light beige powder (the recovered samples is about the 85 wt% of the starting material). In order to verify if the demineralizing procedure altered the polysaccharide, both in the structure and in the molecular weight, infrared spectroscopy measurements and gel permeation chromatography were performed (for experimental details see Section 2.4). In Fig. 1 the IR spectra (height normalized and shifted for clarity) of raw xylan (X) and demineralized xylan (DX) are contrasted. Both xylan samples exhibited similar FTIR spectra, and the typical bands of carbohydrate moieties are present: O–H stretching vibrations ($3600\text{--}3100\text{ cm}^{-1}$), stretching vibrations of C–H and CH_2 groups inside sugar rings (bands around 2900 cm^{-1}), symmetric CH_2 bending vibration (1428 cm^{-1}), C–OH bending mode (around 1050 cm^{-1}), C–H bending mode (1350 cm^{-1}) and OH in-plane vibrations (1270 cm^{-1}) and glycosidic linkages (bands near 1120 cm^{-1} and 1160 cm^{-1} due to the symmetric and asymmetric C–O–C stretchings of β -(1 \rightarrow 4)-glycosidic linkages). In both spectra a peak around 1595 cm^{-1} , typical of furanose units in hemicellulose is found. The presence of a peak at 1740 cm^{-1} in the demineralized xylan FTIR spectrum, ascribable to the COOH group of glucuronic units, confirms the conversion of carboxylate groups into carboxylic groups by the cationic exchange process. The peaks ascribable to carboxylate groups (1570 cm^{-1} (asymmetric COO^- stretch) and 1417 cm^{-1} (symmetric COO^- stretch)) are overlapped with other peaks in the region between 1600 and 1400 cm^{-1} and thus not discernible in the spectrum of the

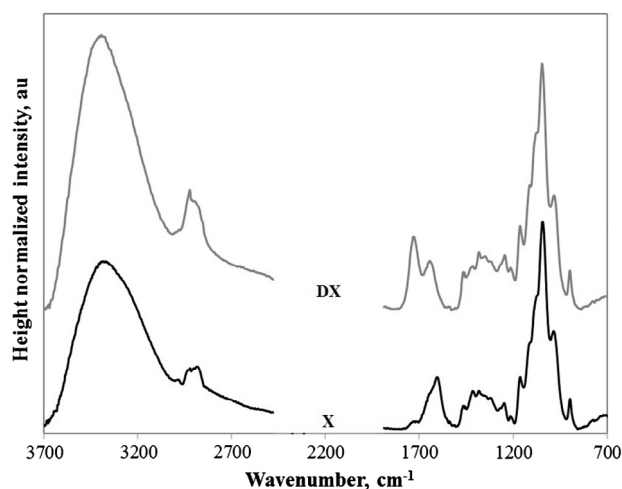


Fig. 1. IR spectra of raw and demineralized xylan samples.

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