

Experimental Investigation on the Effect of K^+ Ions on the Slow Pyrolysis of Xylan

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Pyrolysis is a promising biomass upgrading process for the production of solid, liquid and gaseous fuels. One of the major concerns about biomass utilization is the remarkable variety of its composition in terms of both organic and inorganic matrices, affecting the pyrolysis characteristic temperatures and products yield. The effect of different alkali and earth alkali metals (AAEMs) on biomass and cellulose pyrolysis has been extensively studied, whereas only few works exist concerning the effect of AAEMs on the pyrolysis of the other two main biomass components, namely hemicellulose and lignin. Hemicellulose, which has a carbohydrate nature like cellulose, is expected to be influenced by the presence of AAEMs during the pyrolysis process. In this study, the impact of potassium ions (K^+) on the slow pyrolysis of hemicellulose is assessed using xylan as a representative of hardwood hemicellulose. To this aim, slow pyrolysis tests, up to a temperature of 973 K using a heating rate of 7 K/min, were conducted for xylan samples loaded with K^+ in different amounts. Commercial xylan was demineralized through a cation exchange resin to reduce the presence of inherent inorganics. Subsequently, the demineralized sample was doped with a controlled amount of K^+ (0.3, 0.6 and 1.2 wt.%). The experimental results show that doped and demineralized xylan samples exhibit different pyrolytic behaviors. The initial decomposition temperature of the doped xylan is slightly anticipated with respect to that of the demineralized xylan. Moreover, the gas production is favored at the expense of pyrolysis liquids and the evolution of the release rate of permanent gases (mainly CO_2 and CO) with the temperature is significantly affected by the presence of K^+ .

1. Introduction

In the last decades interest has been increasing towards biomass as renewable source of fuels and materials. The exploitation of biomass as fuel source is strongly supported because a higher sharing of renewable energy use would reduce the dependence on fossil imports in many countries. Moreover, the near-neutral CO_2 emissions from biomass is very attractive since the current systems for capturing CO_2 from fossil fuel plants are still very expensive and represent a serious penalty to the plants energy efficiency. At the same time, the need of a correct disposal of vegetal residues has raised the interest in exploring new routes for the production of bio-based materials from waste biomass (Naik et al., 2010).

Energy carriers and multiple products can be obtained through the thermochemical route (Kambo and Dutta, 2015). Slow pyrolysis is a suitable alternative when high yields of the solid product (char) are required (Giudicianni et al., 2017). Products yield and composition are strongly affected by the relative content of the three main biomass components, i.e., cellulose, hemicellulose and lignin. A lot of work has been carried out to shed light on the slow pyrolysis products composition, in particular when steam has been used as carrier gas (Ragucci et al., 2013; Giudicianni et al., 2014; Gargiulo et al., 2015; Gargiulo et al., 2016). Additionally, because of the catalytic effect, alkali and earth alkali metals (AAEMs) are known to increase solid and gas yields at the expense of liquid yields and have an important role in determining some char characteristics (Giudicianni et al., 2014). Many studies have focused on the effect of AAEMs on pyrolysis, for example the effect of AAEMs on the steam assisted pyrolysis of biomass has been studied by Gargiulo et al. (2015) and

the effect on the slow pyrolysis of cellulose has been studied by Ferreiro et al. (2017); whereas only few works reported about the effect of metals on hemicellulose pyrolysis (Patwardhan et al., 2011; Giudicianni et al., 2018). However, hemicellulose constitutes about 20%-30% of the total mass of annual and perennial plants. A better understanding of the hemicellulose thermal history effect is important to determine the characteristics of biomass char produced by pyrolysis and torrefaction processes. Literature results were typically obtained using commercial xylan as proxy compound for hardwood hemicellulose. Fast pyrolysis studies observed that some mineral species promote the ring-scission (formation of non-condensable gases and light oxygenates) and dehydration reactions (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) (Patwardhan et al., 2011). However, recent experiments conducted on xylan under steam-assisted slow pyrolysis conditions confirmed the role of AAEMs in favoring char and gas production, but highlighted that the formation of light oxygenates via ring scission is preferred instead of dehydration reaction (Giudicianni et al., 2018).

Despite the information that has emerged from the above studies, there are still open questions that need clarification. In this work, a systematic study on the effect of K^+ (one of the main components of inorganic matter in biomass) on xylan slow pyrolysis has been conducted with the aim of enhancing the current understanding of hemicellulose pyrolysis behaviour and to pave the way for formulating more accurate decomposition mechanisms. Pyrolysis measurements were performed following a careful experiment planning aimed at obtaining a high-quality database. To this aim, a complete demineralization of commercial beechwood xylan was performed. After demineralization, xylan was doped with controlled amounts of K^+ ranging from 0 to 1.2 wt.%. The samples were then subjected to pyrolysis tests up to a temperature of 973 K in a pyrolysis reactor, under an inert atmosphere of nitrogen with a heating rate of 7 K/min. The impact of the presence of K^+ is analysed in terms of products yield and gas composition, and the implications on the decomposition pathways are discussed.

2. Materials and methods

Beechwood xylan was purchased from Sigma–Aldrich (X4252) and used as hemicellulose benchmark. First, raw xylan (X) was demineralized following the procedure described in Giudicianni et al. (2018). In brief, raw xylan (~20 g) was dissolved in distilled water (300 mL) and passed through 40 mL of cation-exchange resin (Dowex® 50WX8; H^+ form). The resulting eluate (pH around 2.4) was freeze-dried originating a light beige powder (demineralized xylan sample, DX). The demineralization procedure did not alter the polysaccharide, neither in the structure nor in the molecular weight, as confirmed by the results of infrared spectroscopy measurements and gel permeation chromatography reported in a previous work (Giudicianni et al., 2018). DX was used for pyrolysis tests and to prepare three xylan samples doped with a controlled amount of K^+ (0.3, 0.6 and 1.2 wt.%). In order to dope DX with increasing amounts of K^+ , a K^+ form cation-exchange resin was used. The K^+ form cation-exchange resin was obtained by washing the H^+ form resin with a KOH 1 M solution. A partial K^+ doping of DX was then achieved as follows: 5 g of DX were dissolved in 100 mL of distilled water and passed through 0.5, 2.2 and 10 mL of K^+ form resin to dope the sample with 0.3, 0.6 and 1.2 wt.% of K^+ , respectively. It is worth to note that 1.2 wt.% was the maximum amount of K^+ that was possible to dope using the cation-exchange resin technique and it approximately corresponds to K^+ tightly coordinated with carboxylic functional groups in the xylan moiety. The actual K^+ amount in each sample was evaluated by inductively coupled plasma mass spectrometry (ICP/MS) analysis as reported in a previous work (Giudicianni et al., 2018). The corresponding data are listed in Table 1. A substantial removal of Na^+ and K^+ from the DX sample is obtained through the demineralization process. The actual amounts of K^+ in the doped samples correspond roughly to the nominal amounts.

Table 1: Na^+ and K^+ content of commercial (X), demineralized (DX) and doped xylan samples (DX-K0.3, DX-K0.6, DX-K1.2).

	Na^+ (mg/kg)	K^+ (mg/kg)
X	21510	150
DX	470	0
DX-K0.3	406	2704
DX-K0.6	463	5629
DX-K1.2	470	12060

Demineralized and K doped samples were pyrolyzed at slow heating rate (7 K/min) up to a temperature of 973 K in the pyrolysis reactor used in a previous work (Ferreiro et al., 2017). It consists of a prismatic jacketed

chamber (L = 0.024 m, W = 0.04 m, H = 0.052 m) into which 4 g of biomass are loaded. The sample holder comprises 4 sample trays allocated uniformly along the rectangular cross section of the inner reaction chamber, where biomass is loaded in thin layers (approximately 1 mm thick). A superheater placed before the jacketed reactor heats the carrier gas to the programmed temperature via a PID controller. Carrier gas flows into the jacket at a constant gas mass flow rate (3.09 NL/min), the flow is reversed towards the pyrolysis chamber, passing through a ceramic flow straightener before entering in the chamber. Temperature is monitored using N-type thermocouples along the main dimension of the rectangular sample trays. Pressure transducers monitor the pressure along the carrier gas supply line and at the inlet and outlet of the test chamber.

Condensable products (named hereafter as “liquid”) exiting the reactor flow through a closed loop forced liquid cooling system maintained at 268 K and are collected in a flask submerged in a Dewar filled with liquid Argon (at 87 K). The non-condensable gases were sampled and analyzed after passing through two cotton filter traps and a silica gel trap to remove the residual moisture. Temporal profiles of the release rates of the detected gaseous species evolving from the pyrolysis tests (CO, CO₂, H₂, CH₄, C₂H₄, C₂H₆ and N₂) were obtained by continuously measuring the carrier gas flow rate and by determining the produced gas composition by means of a micro gas chromatograph, equipped with a thermal conductivity detector (Agilent 3000 Quad), every 171.5 s. The yields of the gaseous products were calculated by integrating the measured rate curves along the test duration. At the end of each experimental test the char yield was determined gravimetrically, with respect to the fed sample, using a MS105DU (Mettler Toledo) laboratory balance with 0.01 mg resolution. The liquid yield was evaluated as the amount needed to complete the mass balance. Two replicates of each experiment have been conducted and a relative uncertainty lower than 2% of the average value has been recorded for the obtained products yield.

3. Results

Figure 1 shows the products yield of demineralized and K⁺ doped xylan. The pyrolyzed DX sample mainly produced liquid products (57.0 wt.%), whereas lower yields of char and permanent gases were obtained, 25.1 and 17.9 wt.%, respectively. When the K⁺ content increased from 0 to 1.2 wt.%, the production of char and gas were promoted at the expense of the liquid: char and gas yields increased by 16% and 60%, respectively, at the expense of the liquid yield that decreased by 14%. The increase of K⁺ content from 0.6 wt. % up to 1.2 wt.% did not produce any significant variation in the char yield but favored gas production at the expense of liquid. In that case, gas and liquid yields varied by +36% and -14%, respectively. The overall carbon yield in gas increases with the increase of K⁺ content as seen in Table 2. On the contrary, the carbon yield in char does not have an obvious trend due to the increase of the char yield and the decrease of the carbon content in the chars for increasing K⁺ content.

Table 2: Carbon yield in gas and char from commercial (X), demineralized (DX) and doped xylan samples (DX-K0.3, DX-K0.6, DX-K1.2).

	DX	DX-K0.3	DX-K0.6	DX-K1.2
Carbon yield gas, wt. %	14.1	15.8	16.6	22.3
Carbon yield char, wt. %	51.6	56.8	54.8	51.9

These results are analogous to previous literature findings on the effect of K⁺ on cellulose pyrolysis (Ferreiro et al., 2018). Considering its polysaccharidic nature, hemicellulose was expected to react similarly to cellulose. Xylan is 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. In this study, the increase of char and gas yields with increasing concentration of K⁺ supported, as proposed by Patwardhan et al. (2011), the catalytic role of K⁺ in promoting the ring-scission and rearrangement reactions (formation of non-condensable gases, light oxygenates, and char) in competition with depolymerization and dehydration reactions (leading to higher molecular weight species retaining the xylan pyranose structure like xylose and xylose dehydration products). It is worth noting that while the increase of K⁺ content from 0 to 0.6 wt.% affects the yields of all the pyrolysis products, a further effect only on gas and liquid yields was observed when K⁺ content raised up to 1.2 wt.%. It is likely that both primary and secondary decomposition pathways were affected by the presence of K⁺ ions, and that the effect on the former reached a plateau at lower K⁺ concentration.

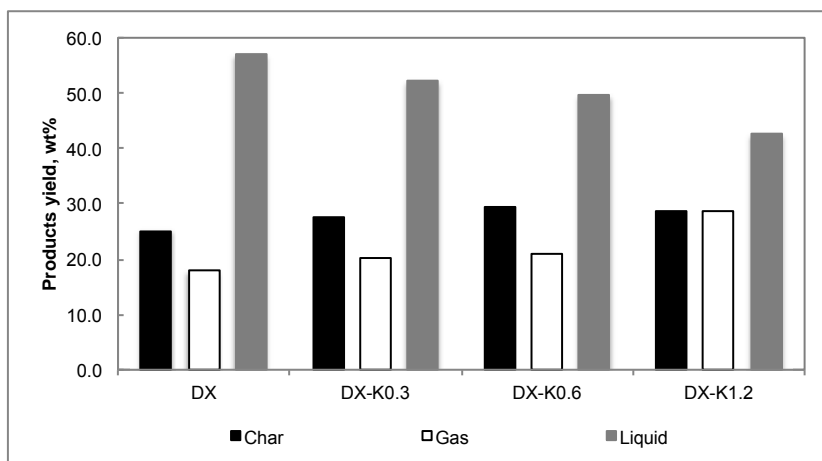


Figure 1: Products yield from demineralized and K^+ doped xylan samples.

To get further insights into the effect of K^+ on the xylan decomposition mechanism, the evolution of the gaseous species along the pyrolysis temperature was studied. The release rate curves of the main gaseous species are shown in Figure 2, while the yields of the major and minor gaseous species from demineralized and K^+ doped xylan are shown in Figure 3. DX decomposed releasing CO_2 and CO as main gaseous species, with CO_2 being the predominant species. The CO_2 and CO curves shown in Figure 2 allowed distinguishing two overlapped thermochemical events. The first event, in the lower temperature region, ranging between 423 to 580 K represents the main peak on both the release rate curves. In the lower temperature region, CO_2 could result from the decomposition of carboxylic moieties on the 4-O-methyl glucurono-xylan units whereas a number of chemical pathways could account for the formation of CO, such as the decomposition of carbonyl ending groups left from the dehydration reactions of the side chain groups and secondary decomposition of fragments containing aldehydes structure (Shen et al., 2010). In the upper temperature region, namely between 580 and 873 K, a second decomposition event occurred, resulting in a shoulder on the decreasing branch of the CO_2 release rate curve and the increase of the CO release rate with the maximum occurring at about 645 and 672 K, respectively.

The production of H_2 and CH_4 was observed for higher temperatures. It is likely that the release of these species at higher temperature derives from reactions occurring after the opening of the xylan ring. The release rate of CH_4 shows a non-monotonic trend and presented a maximum at about 783 K, whereas the H_2 release rate increased with temperature up to 973 K.

The introduction of K^+ into the demineralized sample affected significantly the release rate of the measured gaseous species, suggesting that the decomposition mechanisms were modified in the presence of K^+ . By increasing the K^+ content up to 0.3 wt.%, the CO_2 release rate increased in the lower temperature region, whereas the peak in the upper temperature region remains unchanged. Overall, the CO_2 yield increased from 12.9 to 15.2 wt.% (see Figure 3a) due to the enhancement of CO_2 release in the low temperature region. As shown in Figure 2, the first peak of CO_2 release rate curve was only slightly affected by the further addition of K^+ , whereas the second peak remains unchanged. Accordingly, a further increase of K^+ content up to 0.6 wt.% did not affect the CO_2 yield. At a higher concentration of K^+ , both the first and the second peak in the release rate curve were observed to increase. Further investigations on the yields of the main liquid species are necessary to go deep into the interpretation of the overall effect of K^+ on thermochemical CO_2 release.

The presence of K^+ clearly enhanced the CO release rate at lower temperatures, where CO is mainly released by the carbonyls left from dehydration reactions of side chain groups. On the contrary, the presence of increasing amounts of K^+ had the opposite effect in the upper temperature region after the occurrence of opening ring reactions, even though the more significant effect was obtained on going from 0 to 0.3 wt.% of K^+ . Overall, for K^+ concentration up to 0.6 wt.% the promotion of CO release in the lower temperature region was counterbalanced by the reduced CO release at higher temperatures (see Figure 3a). At higher concentrations of K^+ , the CO yield increased from 3.8 wt.% to 4.7 wt.%. In the high temperature region, the presence of K^+ enhanced the CH_4 and H_2 release rates, thus suggesting a catalytic effect of K^+ also on secondary reaction pathways. This resulted in higher yields of CH_4 , C_2H_6 and H_2 .

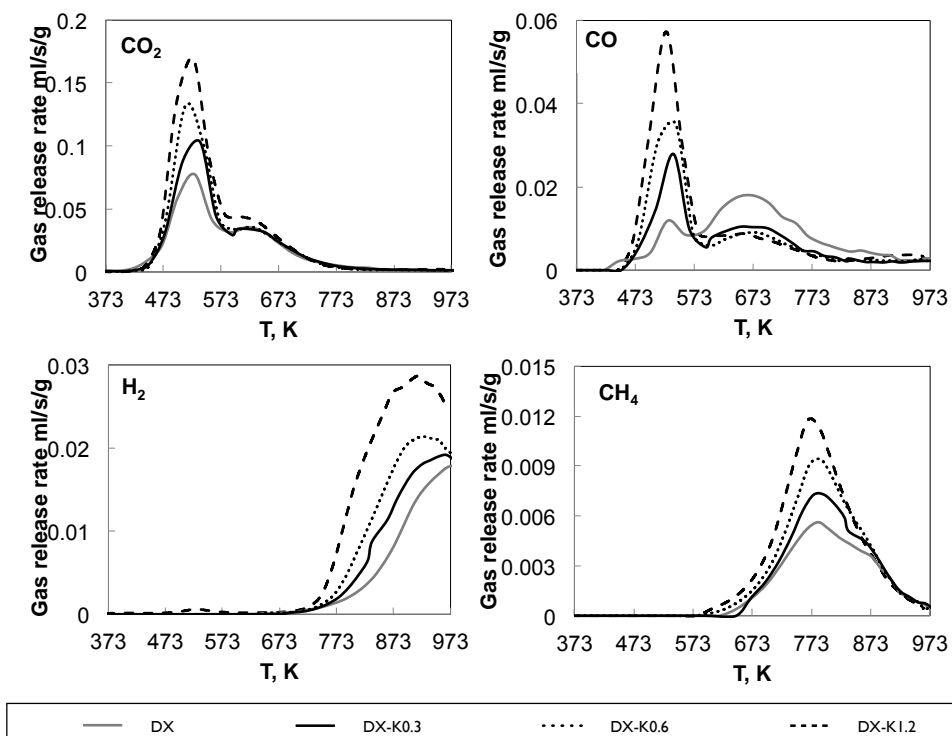


Figure 2: Release rate profiles of the main gaseous species along the temperature produced from demineralized and K^+ doped xylan samples.

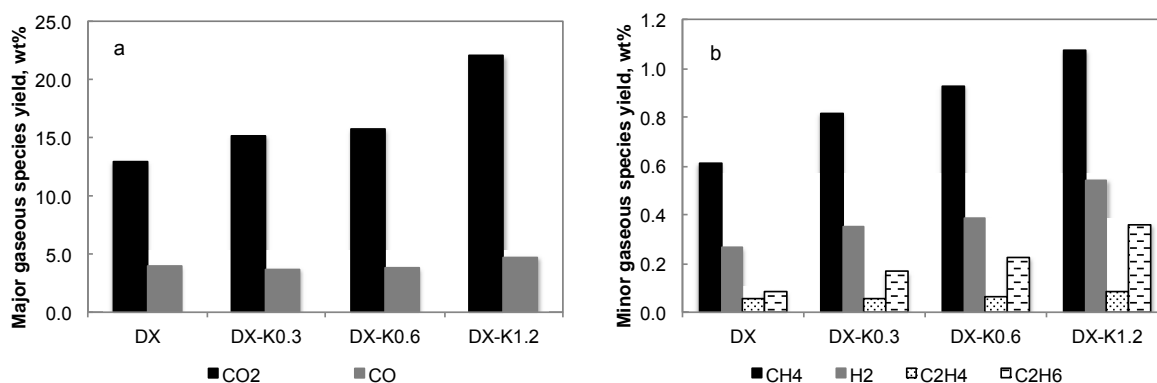


Figure 3: Yields of the major (a) and minor (b) gaseous species from demineralized and K^+ doped xylan samples.

4. Conclusions

The influence of potassium ions on the slow pyrolysis of hemicellulose was studied using commercial xylan as proxy compound. The thermal behavior of doped xylan samples at increasing concentration of K^+ from 0 to 1.2 wt.% was studied in an atmospheric pyrolysis reactor, in nitrogen, under a slow heating rate (7 K/min). In the whole temperature range (373-973 K) the presence of K^+ affected both the primary and secondary decomposition pathways. Overall, increasing the K^+ concentration up to 1.2 wt.%, promoted the gas production at the expense of the liquid production, mainly due to the higher CO₂ yields. However, the analysis of the release rate curve of CO₂ and CO revealed the influence of K^+ addition on the competition between different reaction pathways. Further experimental tests at intermediate concentrations of K^+ and characterization of the main liquid compounds are currently in progress to obtain a better understanding of the effect of K^+ on the specific decomposition mechanisms.

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