

# **SLOW PYROLYSIS OF POTASSIUM DOPED XYLAN: A COMPARISON BETWEEN TWO DOPING APPROACHES**

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## **Abstract**

In this study, the effect of potassium ions on the slow pyrolysis of hemicellulose is assessed using xylan as a representative of hardwood hemicellulose. Thermogravimetric and pyrolysis tests, up to 973 K at a heating rate of 7 K/min, were conducted on different xylan samples: commercial xylan (X), demineralized xylan (DX), potassium doped xylan (DX\_K) samples. Commercial xylan was demineralized through a cation exchange resin in order to reduce the presence of inherent inorganics. Subsequently, the demineralized sample was doped with a controlled amount of K ions (ca 1 wt%) by using two different approaches: wet impregnation and cation-exchange resin.

The results show that the wet impregnation doping procedure affected negligibly the pyrolytic behavior of the demineralized sample, and thus it is not suitable for the study of the effect of salts ions on xylan pyrolysis.

By comparing the results obtained from X, DX and \_K doped DX through cation exchange method, it can be inferred that, overall, the presence of metal ions favored the gas production at the expense of pyrolysis liquids and the release rate of permanent gases (mainly CO<sub>2</sub> and CO) along the temperature is greatly altered too.

## **Introduction**

The interest in the exploitation of biomass as fuel source increased in the last decades due to biomass neutrality with respect to CO<sub>2</sub> emissions. At the same time, the need of a correct disposal of vegetal residues raised the interest in exploring new routes for residual biomasses valorization [1].

Energy carriers and added-value products can be obtained through biomass thermochemical conversion [2]. Products yield and characteristics are strongly affected by the relative content of organic and inorganic biomass components [1].

There are several studies focused on the effect of the inorganic matter on biomass pyrolysis showing that the presence of alkali and earth alkali metals (AAEMs) causes an increase in the yields of char and gas at the expense of pyrolysis liquids (favoring dehydration, demethoxylation, decarboxylation reactions).

A wide literature is available on the effect of AAEMs on pyrolysis of biomass and cellulose, whereas only few works reported about the effect of metals on hemicelluloses pyrolysis [3,4]. However, hemicelluloses constitute about 20–30%

of the total mass of annual and perennial plants and the comprehension of their thermal behavior is important for determining the characteristics of biomass char and even more of torrefied biomass. Recent experiments conducted on xylan under slow pyrolysis conditions in presence of steam 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 [4].

In order increase the comprehension of the effect of metal ions on hemicellulose pyrolysis behavior and to pave the way for the formulation of possible decomposition mechanisms a study on the effect of K ions (one of the main components of inorganic matter in biomass) on xylan slow pyrolysis was carried out. To this aim a complete demineralization of commercial beechwood xylan was performed. After that the demineralized xylan was doped with about 1 wt.% of K<sup>+</sup> ions by using two different approaches: wet impregnation and cation-exchange resin. The resulting samples, the commercial and the demineralized xylan samples were subjected to pyrolysis tests up to 973 K under an inert atmosphere of nitrogen at a heating rate of 7 K/min and the products yields and gas composition were compared.

### **Experimental section**

*Materials.* Beechwood xylan (Sigma–Aldrich X4252) was used as hemicellulose representative. Raw xylan (X) was demineralized as described in [4]. A significant removal of the metal ions in the demineralized sample (DX) was obtained through the demineralization procedure (the ash content decreased from 4.4% to 0.3%).

DX was doped with a controlled amount of K<sup>+</sup> ions (~1 wt.%) in two different ways. The first procedure was to pass the DX sample through a K<sup>+</sup> form cation-exchange resin: 5 g of DX were dissolved in 100 mL of distilled water and passed through 10 mL of K<sup>+</sup> form resin. Then, the sample was dried at 50 °C for 24 hours. The second doped sample was prepared according to the wet impregnation procedure: the appropriate amount of KCl (about 191 mg) was dissolved in 100 mL of deionized water and added to 5 g of DX. The suspension was stirred for 30 min at ambient temperature to obtain a well-mixed slurry and dried in an oven at 50 °C for 24 hours.

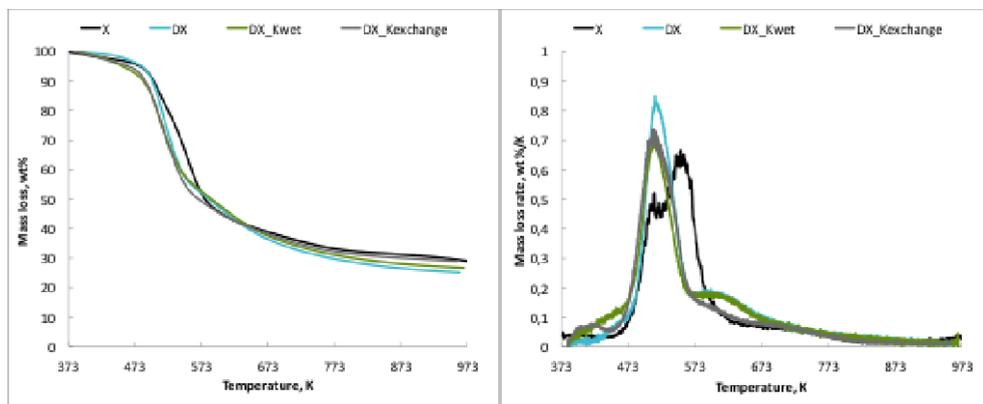
*Thermogravimetric tests.* The thermal behavior of the samples was studied in a thermogravimetric (TG) apparatus (STA 449 F5 Jupiter) by heating the sample (2–10 mg) from 323 K up to 973 K, at atmospheric pressure under an inert environment (N<sub>2</sub>, 50 mL/min at a heating rate of 7 K/min).

*Pyrolysis tests.* Commercial, demineralized and K<sup>+</sup> doped samples were pyrolysed at 7 K/min up to 973 K in the reactor described in detail elsewhere [4–6]. Briefly, it consists of a steel jacketed prismatic chamber in which the sample (4–6 g) is spread in thin layers (approximately 1 mm thick) over 4 sample trays, placed uniformly along the rectangular cross-section of the reaction chamber. 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) and then its flow is reversed so that it enters the reaction environment through a ceramic flow straightener. The residence time of the gas in the reaction chamber is 2 s, thus limiting the secondary reactions of the volatiles evolving from the primary decomposition of the feedstock. Temperature is monitored using N-type thermocouples along the main dimension of the rectangular sample trays. The gaseous stream that exits the reaction chamber passes through a condensation device. The non-condensing gases are fed to a micro gas chromatograph, equipped with a thermal conductivity detector (Agilent 3000 Quad) to obtain temporal profiles of the release rates of all the gaseous species evolving from the pyrolysis tests (CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and N<sub>2</sub>). 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 char yield was determined gravimetrically, with respect to the fed sample. The liquid yield was evaluated as the amount needed to complete the mass balance.

### Result and discussion

*Thermogravimetric results.* Figure 1 shows the experimental TG profiles of the samples and the corresponding DTG curves.

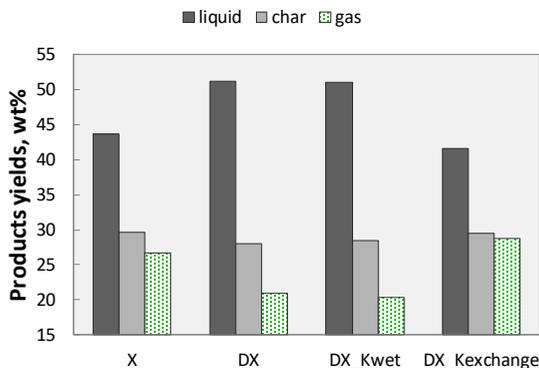


**Figure 1.** TG (left) and DTG (right) profiles of the samples.

As indicated by the TG profile, X decomposed between 473 K and 623 K, and two distinct peaks can be detected at 510 K and at 550 K, respectively. Demineralized xylan decomposed over a narrower temperature range (473–573 K) with the main peak occurring at 517 K. A second small peak is detected between 560 and 660 K. As concerns the char yields, in the case of the X sample, a higher amount of solid residue compared to the DX sample was obtained (29.7 wt.% for X and 25.5 wt.% for DX). The doped sample obtained by wet impregnation (DX<sub>Kwet</sub>) decomposed following the same TG profile of DX with a main event peaked at 513 K and small event detected between 560 and 660 K. The char yield was 26.8 wt.%, but the slight difference with respect to X char yield is within the experimental error. The DTG profile of the doped sample obtained by cation-exchange (DX<sub>Kexchange</sub>)

resembled the DX profile except for the absence of the second event between 560 and 660 K. The char yield was 29 wt.%, higher than that of DX and DX<sub>K<sub>wet</sub></sub>.

*Pyrolysis products distribution.* Figure 2 shows the pyrolysis product yields of all the xylan based samples.



**Figure 2.** Pyrolysis products yields.

As expected, the demineralization process clearly favored the liquid production at the expense of gas (the gas yield decreased from 26.7 in X to 20.9 wt% in DX, while the liquid yield increased from 43.7 in X to 51.1 wt.% in DX) and affected slightly char production (the char yield passes from 29.6 in X to 28 wt.% In DX).

K doping through wet impregnation did not produce noticeable changes in the product yields compared to DX. On the contrary, char and gas production at the expense of the liquid was promoted in DX<sub>K<sub>exchange</sub></sub> in agreement with previous literature findings on the effect of K<sup>+</sup> ions on cellulose pyrolysis [6].

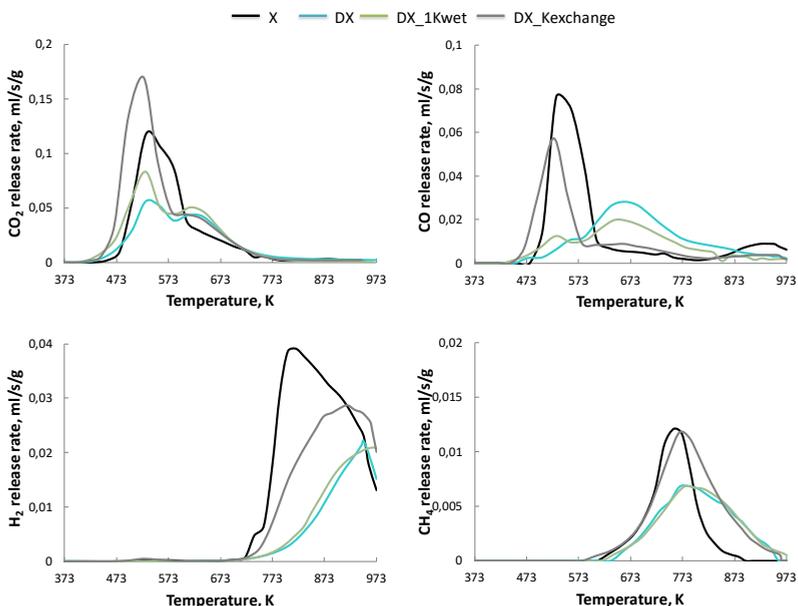
It is likely that K<sup>+</sup> promoted the ring-scission and rearrangement reactions (formation of non-condensable gases, light oxygenates, and char) in competition with depolymerization and dehydration reactions leading to higher molecular weight species retaining the xylan pyranose structure (xylose and xylose dehydration products) [3]. In order to get useful insights into the effect of K<sup>+</sup> ions on xylan decomposition mechanisms, the evolution of the gaseous species along the pyrolysis temperature was studied. The release rate curves of the main gaseous species (CO<sub>2</sub>, CO, H<sub>2</sub> and CH<sub>4</sub>) are shown in Figure 3.

For all the samples, CO<sub>2</sub> and CO were the main gaseous species, even though the production of CO<sub>2</sub> was predominant with respect to CO. CO<sub>2</sub> mainly resulted from decomposition of side acetyl groups and carboxylic groups, whereas CO derives from the carbonyl ending groups left from the dehydration reactions of the side chain groups [3].

For the X sample, CO<sub>2</sub> curve was characterized by two overlapped events in the lower temperature region (470–600 K), whereas two distinct events can be detected for DX sample: the first one between 423 and 580 K and the second one in the 580–873 K temperature range.

The release of CO from X sample exhibited a main release peak centered at 558 K,

whereas in the case of DX sample two overlapped events in the same temperature ranges as CO<sub>2</sub> were detected, but the first one is a shoulder on the increasing branch of the second main peak.



**Figure 3.** Release rate profiles along the temperature of the main gaseous species produced from the different xylan samples.

The introduction of K<sup>+</sup> ions into the demineralized sample by wet impregnation did not induce great modifications on the decomposition mechanism of DX except for a slight enhancement of the first peak of CO<sub>2</sub> release rate. On the contrary, the K<sup>+</sup> doping through cationic exchange resin induced great modifications on the release rate of all the detected gaseous species. In both CO<sub>2</sub> and CO release rate curves the enhancement of the first event in the 423-580 K temperature range was observed, whereas only for CO release rate curve the depression of the second peak occurred. For all the samples, minor species such as H<sub>2</sub> and CH<sub>4</sub> were released at higher temperature, at about 750 and 650 K, respectively, probably derived from reactions occurring after the opening of the xylan ring. Both for X and DX\_K<sub>exchange</sub> samples the release of these two species is slightly anticipated with respect to DX and DX\_K<sub>wet</sub> sample.

Overall, the presence of metal ions in X and K<sup>+</sup> in DX\_K<sub>exchange</sub> samples favored the release of all the gases with particular effect on CO<sub>2</sub>, H<sub>2</sub> and CH<sub>4</sub>. The enhanced release of H<sub>2</sub> and CH<sub>4</sub> denote a slight catalytic effect of K<sup>+</sup> also on secondary reaction pathways.

The structural features of xylan can clarify the contrasting results obtained with the two doping procedures used in this study. The xylan is an acidic polysaccharide

containing one glucuronic unit approximately for ten xylan units, so the cation-exchange procedure allowed the complete exchange between the  $H^+$  and  $K^+$  transforming the COOH groups of glucuronic unit in  $COO^-K^+$  form. In this way the  $K^+$  ions are tightly linked to xylan polysaccharide and can properly exploit their catalytic effect. On the contrary, the wet impregnation procedure with KCl does not allow the exchange between the  $H^+$  and  $K^+$  and thus the catalytic effect is lowered.

### Conclusions

In the present paper the influence of  $K^+$  ions on hemicellulose pyrolysis was studied using commercial xylan as proxy compound. The thermal behavior of commercial, demineralized xylan and  $K^+$  doped samples obtained with two different doping procedures was investigated in a pyrolysis reactor in nitrogen atmosphere at atmospheric pressure under slow pyrolysis conditions (HR= 7 K/min). The demineralization process clearly favored the liquid production at the expense of gas and slightly reduced char production. The two doping approaches produced contrasting results. Doping through wet impregnation did not produce noteworthy modifications either on product yields or gas release rate. On the contrary, sample doped through cation exchange resin produced higher gas yield at the expense of liquid yield similarly to what observed for commercial xylan rich in inorganic matter. In this case also the mechanisms responsible of the release of the main gaseous species were greatly affected by the presence of  $K^+$ .

In the case of xylan the wet impregnation is not the suited doping procedure, probably because of the chemical nature of the polysaccharide (low molecular weight and rich in COOH).

Overall, the results obtained in this work about the  $K^+$  effect encourage future researches for the production of a database useful for the improvement of the predictive capabilities of pyrolysis kinetic models also in presence of metal ions.

### Acknowledgments

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