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# Effect of KCl Doping on the Slow Pyrolysis of Lignin

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This study examines the effect of KCl on the slow pyrolysis of lignin. Commercial alkali lignin was chosen as reference compound and it was demineralized through a washing procedure using two different leaching media, distilled water and a HF water solution at 3 wt.%. The ICP/MS analyses of the demineralized samples showed that the HF washing procedure was more effective than the water washing in reducing the K ions contents of the raw lignin. The HF demineralized sample was doped with an amount of KCl corresponding to 0.6 wt.% of K ion using the wet impregnation procedure. Subsequently, thermogravimetric (TG) analysis and slow pyrolysis tests of raw, demineralized and doped lignin samples were performed at a heating rate of 5 °C/min up to 900 °C and 700 °C, respectively. Gas species release was monitored along the pyrolysis temperature. The reduction of K ions slightly affected the pyrolytic behaviour of the raw sample by delaying both the onset of the lignin decomposition reactions and the maximum weight loss rate by about 10 °C. Moreover, the reduction of the alkali metals content enhanced the weight loss in the range of 330 and 450 ºC, thus affecting only negligibly the solid residue yields at 700 °C. Finally, it was observed that the KCl addition promotes decarboxylation reactions and dehydrogenation of the char matrix and depresses the carbon monoxide production.

## 1. Introduction

Pyrolysis is a promising biomass upgrading process capable to produce solid, liquid and gaseous products suitable to be used as fuels, sources of chemicals and low-cost materials for a wide range of applications. The numerical modeling of biomass pyrolysis is a challenging topic, because biomass is a complex material and it requires a detailed characterization in terms of both organic and inorganic matrices. Alkali metals in ion-exchangeable (salts or organically bound compounds) or mineral forms, which are particularly abundant in herbaceous biomass, cannot be neglected given their proven effect on both pyrolysis decomposition mechanisms and products characteristics (Eom et al., 2012). The different speciation and phases, under which the inorganics are present in biomass, make difficult to understand the extent of their catalytic activity on specific reaction pathways. A simplified approach consists in assessing the effect of inorganics separately on the biomass organic components (cellulose, hemicellulose and lignin). However, this approach poses a further level of complexity when hemicellulose and lignin are considered, since their chemical structures are more complicated than the cellulosic polymer, and due to the existence of different kinds of hemicelluloses and lignins and different extraction methods. Lignin is a racemic heteropolymer consisting of three hydroxycinnamyl alcohol monomers differing in their degree of methoxylation: p-coumaryl, coniferyl and sinapyl alcohols. The content of p-coumaryl, coniferyl and sinapyl alcohol in lignin is dependent on the feedstock. Alkali lignin and Klason lignin are isolated by removing holecellulose using alkali and acid solutions, respectively. Organosolv lignin is obtained extracting lignin with an ethanol/water mixture, whereas milled wood lignin is isolated by milling biomass in a ball mill adding neutral organic solvents. The lignin isolation method determines the fate of the lignin's weak ether linkages and side branches. Due to the mild extraction procedure (Wang et al., 2015), alkali lignin was often used as proxy compound in experimental studies with the aim of creating databases for modelling pyrolysis kinetic mechanisms. Some work on the effect of Na ions was performed due to the presence of this cation as residue of the alkali extraction procedure (Jakab et al.,

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1997). The presence of Na ions were proven to catalyze the rupture of ether bonds and side chain units thus promoting the production of low molecular weight species at the expense of condensed aromatic molecules. Decarboxylation and dehydration reactions are promoted by the presence of Na ions, thus leading to lower amounts of oxygen at high temperature. They favor the decarbonylation and dehydrogenation reactions at high temperature. Moreover, Na ions seem to exert their catalytic activity also on the decomposition mechanism of methoxy groups bound to the aromatic structures.

Despite the great interest in Na ions, it is worth to note that biomass contains typically higher amounts of Ca and K ions (Phyllis2 database), but only few studies report on their effect on alkali lignin pyrolysis. In this work, commercial alkali lignin, containing high amounts of Na ions, was demineralized and then doped with KCl. The thermal behavior of raw, demineralized and KCl doped samples was studied through thermogravimetric analysis (TGA) up to 900 °C and pyrolysis tests up to 700 °C, at a heating rate of 5 °C/min. Weight loss profiles, products yields and gas release rates as a function of the temperature have been compared and the catalytic effect of this salt on the main decomposition pathways was elucidated.

## 2. Materials and methods

Lignin alkali from Sigma Aldrich (referred in the following as Lignin) was used as lignin reference compound. The sample was demineralized using two washing solutions, distilled water (Lignin D-W) and a 3 wt.% HF solution (Lignin D-HF) following the procedure described in Eom et al. (2012).

The ash content of the raw and the two demineralized samples was measured with a TGA701 LECO analyzer following the ASTM E870 procedure to evaluate the effectiveness of the demineralization procedure. The content of the major inorganic elements in the three lignin samples was determined by means of inductively coupled plasma mass spectrometry (ICP/MS) using an Agilent 7500CE instrument after microwave-assisted acid digestion based on US-EPA methods 3051 and 3052. Table 1 shows the results of both analyses. Lignin is characterized by a high content of Na ions retained in the sample after the extraction with a NaOH solution. The concentration of K ions is one order of magnitude lower than the Na ions concentration, even though the typical concentration of this ion in the original biomass could be significantly higher (Tortosa Masiá et al., 2007). The HF demineralizing solution was more effective in reducing the ash content. The concentration of alkali ions, K and Na, was reduced by 93% and 98%, respectively, whereas the distilled water removed only 79% and 51% of K and Na ions, respectively. Both demineralizing solutions did not alter the concentration of the earth alkali ions (Table 1).

*Table 1: Effect of demineralization procedure on the main inorganics concentrations. Data reported on dry basis (db).*

| | Ash, wt.% | Na, ppm | K, ppm | Mg, ppm | Ca, ppm |
|---|---|---|---|---|---|
| Lignin | 2.37 | 5954 | 650 | 120 | 334 |
| Lignin D-W | 0.94 | 1232 | 317 | 133 | 339 |
| Lignin D-HF | 0.07 | 105 | 44 | 134 | 351 |

Lignin D-HF was chosen for preparing the KCl doped sample (Lignin K) following the wet impregnation procedure (Van Lith et al., 2008) using an aqueous solution of KCl corresponding to a concentration of K ions of 0.6 wt.% and a biomass to water ratio of 1:10. The doping concentration produced a sample with a K ion concentration comparable to the one of Lignin. The mixture was stirred for 30 min at ambient temperature and dried at 70 °C for 24 h and then at 105 °C for 2 h to remove the moisture.

In order to verify that the demineralization procedure did not altered the chemical structure of the polymer, Fourier Transform Infrared Spectroscopy (FTIR) measurements of Lignin and Lignin D-HF were performed and the IR spectra in the 650-4000 $cm^{-1}$ range were recorded on a Perkin-Elmer MIR spectrophotometer in transmittance mode. The spectra were acquired on KBr pellets (1 wt. %) collecting 32 scans and correcting the background noise. In Figure 1 the IR spectra (height normalized and shifted for clarity) of Lignin and Lignin D-HF are compared. Both the spectra are comparable and both of them exhibited the typical bands of ligninic moieties (Gargiulo et al., 2016), confirming that the demineralization process with diluted HF does not alter the polymer structure.

Thermogravimetric analyses (TGA) of Lignin, Lignin D-HF and Lignin K were performed with a Perkin-Elmer STA6000 thermogravimetric analyzer under inert atmosphere (nitrogen) at 5 °C/min up to 900 °C. Pyrolysis tests of all samples were performed under the same TGA operating conditions up to 700 °C in the pyrolysis reactor described by Gargiulo et al. (2018). It consists of a prismatic jacketed chamber (L = 0.024 m, W = 0.04 m, H = 0.052 m) into which 6 g of a sample are loaded on 4 sample trays in thin layers (approximately 1 mm thick) and distributed uniformly along the rectangular cross section of the inner reaction chamber.

Temperature is monitored using N-type thermocouples in two cross sections at the beginning and end of the sample trays to verify the absence of temperature gradients inside the reactor. Nitrogen flows along the sample trays (3.09 NL/min) and the sample is heated at 5 °C/min.

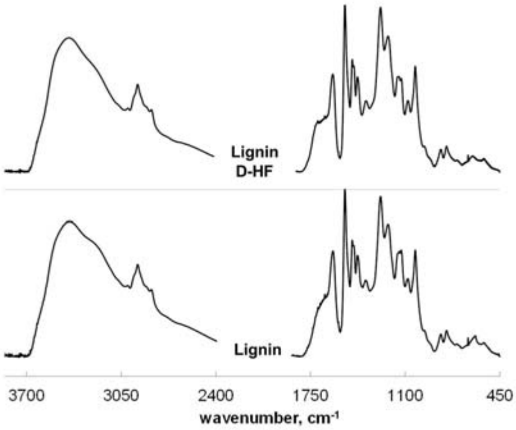

*Figure 1: FTIR spectra of Lignin and Lignin D-HF.*

The gaseous products exiting the reactor flow through a closed loop forced liquid cooling system maintained at 5°C and then through a flask submerged in a dewar filled with liquid nitrogen at -196 °C, where the condensable species are collected. The non-condensable gases were sampled and analysed by means of a micro gas chromatograph, equipped with a thermal conductivity detector (Agilent 3000 Quad), every 171.5 s. Temporal profiles of the release rates of the detected gaseous species (CO, $CO_2$, $H_2$, $CH_4$, $C_2H_4$, $C_2H_6$ and $N_2$) were obtained by continuously measuring the carrier gas flow rate and by determining the produced gas composition. 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. The liquid yields were evaluated as the amount needed to complete the mass balance. Two replicates of each experiment have been conducted and a relative error lower than 0.5% of the average value has been recorded for the obtained products yield.

## 3. Results and discussion

### 3.1 TGA test

Figure 2 shows the TG and DTG curves of Lignin, Lignin D-HF and Lignin K. All the samples show a sharp mass loss stage between 250 and 450 °C, where most of the volatiles are released. Afterwards, the TG curves decayed smoothly up to 900 °C. According to the structural characterization of alkali lignin extracted from pine (Wang et al., 2015), the ether bonds and side branches in the original lignin are well-preserved after alkali extraction. Because of their low thermal stability, they are easily decomposed from about 250 °C and the devolatilization of the resulting species are responsible for the peak in the DTG curves.

The peak of the DTG curve slightly increases after the demineralization and it decreases with respect to the Lignin D-HF sample after KCl doping. Consistently, the yield of the solid residue of Lignin D-HF is lower than the ones obtained for Lignin and Lignin K. Moreover, the peak of the weight loss curve of Lignin D-HF is delayed for about 10 °C with respect to the peaks of Lignin and Lignin K. Note that doping the sample with KCL inhibited the peak occurring between 600 and 700 °C observed for the raw and demineralized sample. In fact, the inhibition of this peak compensates for a higher lower temperature peak of Lignin K as compared to Lignin D-H, leading to a similar char yield.

Even though the K ion concentrations in the Lignin and Lignin K samples are comparable Lignin contains also a great amount of Na ions. As previously observe by Jakab et al. (1997), in the low temperature region (250-450 °C) Na catalyses the cleavage of the ether bonds between the aromatic rings and in the short branches bonded to the aromatic structures. It is likely that in Lignin a synergic effect of Na and K ions enhanced the decrease of the main peak in the DTG curve with respect to Lignin K.

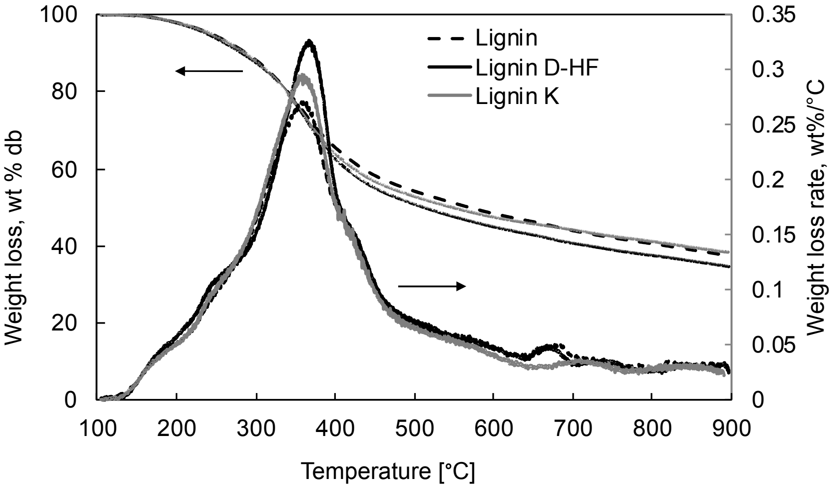

*Figure 2: TG and DTG curves of Lignin, Lignin D-HF and Lignin K (db).*

### 3.2 Pyrolysis tests

Figure 3 shows the products yields on dry ash free (daf) basis of the pyrolysis tests of Lignin, Lignin D-HF and Lignin K. The yields of the organic fraction of the chars are shown for evaluating the effect of KCl on the pyrolytic behavior of the organic matrix of the lignin.

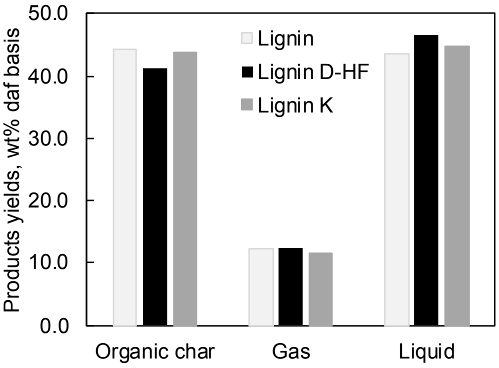

*Figure 3: Products yields of Lignin, Lignin D-HF and Lignin K (daf basis).*

The organic char yield slightly decreases after the demineralization and increases again after the KCl doping in agreement with the trend observed for the solid residue obtained at 900 °C in the TG experiments. The opposite behavior is observed for the liquid yields, whereas the variations of the gas yields are within the experimental error. Trubetskaya et al. (2020) showed a similar trend for $KNO_3$ doped lignin under fast pyrolysis conditions. As explained in the previous section, K ions can catalyse the rupture of branches and ether bonds contrasting the formation of oligomers and polymers in favour of low molecular weight liquid species.

The mild effect of KCl on char and liquid yields can be explained by the inefficient contact between the salt molecules and the lignin samples, as was previously observed also for slow pyrolysis of KCl and NaCl doped xylan (Gargiulo et al., 2019) and for fast pyrolysis of NaCl doped lignin (Jakab et al, 1997). In these studies, the wet impregnation and the mechanical mixing doping procedures were found to be less effective then cationic-exchange approach.

The synergic effect of K and Na ions in Lignin is negligible since it did not produce relevant differences between the products yields of Lignin and Lignin-K samples. This is in agreement with the comparable solid residues obtained at 900 °C in the TG experiments since an increase of alkali ions content corresponds to an increase of the counterions content and speciation. A role of the anionic counterions ($Cl^-$ for Lignin K and $OH^-$ and $CO_3^{2-}$ for Lignin, Guo et al., 2012) acting as a slight inhibitor of the catalytic effect of K and Na ions cannot be excluded. This effect is well documented for salt-doped cellulose in Patwardhan et al. (2010).

The composition of the gas shown in Figure 4 (panels a and b) and the temperature evolution of the main gaseous species shown in Figure 5 (panels a-d) provide insights to the decomposition mechanisms affected by the presence of KCl. The gas phase products from Lignin and Lignin K pyrolysis are richer in $CO_2$ and $H_2$, poorer in CO, whereas $CH_4$ and $C_2$ are only negligibly affected by both demineralization and KCl doping.

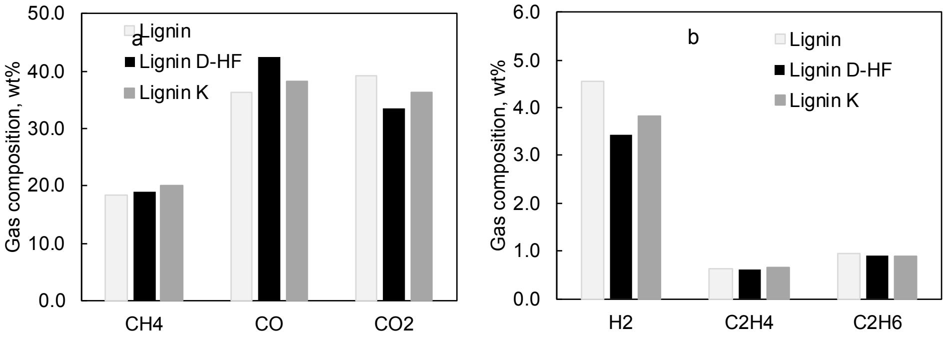

*Figure 4: Gas composition of Lignin, Lignin D-HF and Lignin K: (a) $CH_4$, CO and $CO_2$, (b) $H_2$, $C_2H_4$ and $C_2H_6$.*

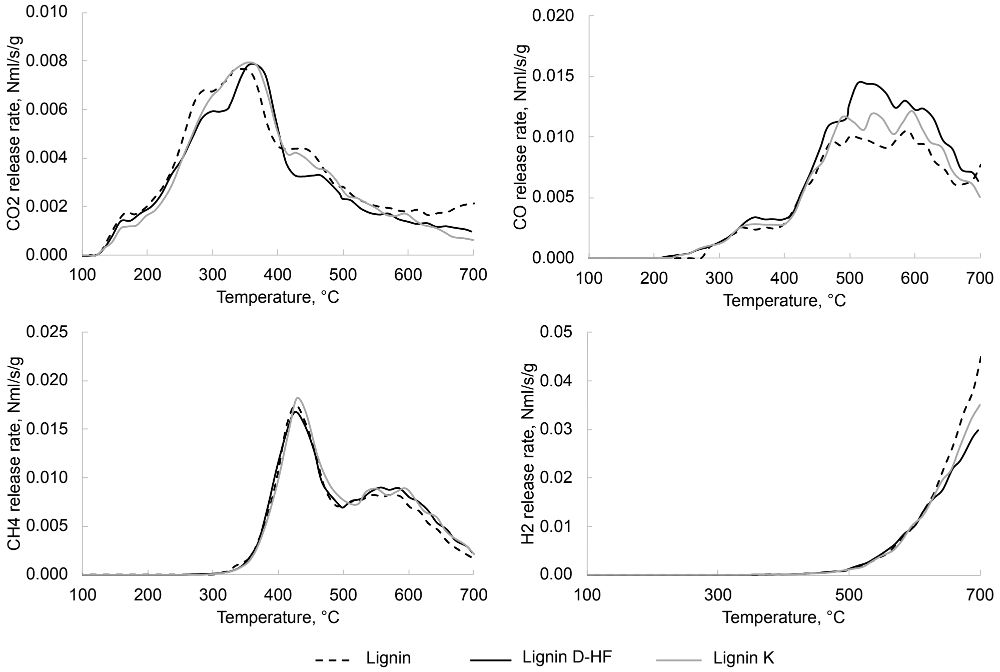

*Figure 5: Release rate of (a) $CO_2$, (b) CO, (c) $CH_4$, and (d) $H_2$ for Lignin, Lignin D-HF and Lignin K.*

The qualitative trends of the release rate of the main gaseous species were similar for the three lignin samples. Both $CO_2$ and CO are released in a broad temperature range. $CO_2$ derives mainly from the decomposition of carboxyl and ester groups (Wang et al., 2015); its release rate has one main peak between 355 and 370 °C and two minor shoulders on both the increasing and decreasing branches of the release rate curve. The addition of KCl and the simultaneous presence of K and Na ions in Lignin promotes the decarboxylation reactions producing an increase of the two shoulder peaks in the $CO_2$ release rate curve.

CO starts to release at higher temperature than $CO_2$ and from 400 °C onwards several peaks of comparable intensity are observed indicating different routes for carbonyls decomposition. Alkali ions in Lignin and KCl in Lignin K depress the decarbonylation reactions leading to the formation of CO.

The release of $CH_4$ produces a first main peak at 350-500 °C and a second shoulder peak at 550-650 °C. The first peak mainly results from the fragmentation of aliphatic side branches and partly from the demethylation of methoxy groups, while the second one, having a broad evolution profile, can be attributed to the charring reactions occurring at high temperatures (Jackab et al., 1993). As observed also for NaCl doped lignin (Jakab et al. 1997), the methane release profile is not affected by the presence of KCl probably because of the less efficient contact with respect to the organically bound alkali ions (Jakab et al., 1997).

In the high temperature region, when most of the oxygen is already removed from the organic matrix, charring reactions proceed via dehydrogenation reactions, which are responsible for the steep increase of the $H_2$ release rate curve favored by the addition of KCl and even more in the Lignin sample with a higher content of alkali ions.

## 4. Conclusions

The addition of KCl to demineralized alkali lignin has a slight effect on the pyrolysis mechanisms. The results of this study showed that KCl inhibited the production of liquid at the expense of char, producing a variation of the char and liquid yields of about 8% under the conditions of this study. Deoxygenation, occurring through $CO_2$ production, was promoted in the low temperature region, whereas above 450 °C the production of CO was depressed and the charring reactions leading to $H_2$ production were enhanced. However, the observed variations in gas composition are lower than 10%. Further experiments with higher KCl amounts attaining the typical values of K ions in herbaceous biomasses are needed to assess the importance of the catalytic effect on lignin in real biomass. Moreover, liquid products should be characterized to get further insights into the decomposition mechanisms affected by alkali ions.

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### References

Eom I.Y., Kim J.Y., Kim T.S., Lee S.M., Choi D., Choi I.G., Choi J.W., 2012, Effect of essential inorganic metals on primary thermal degradation of lignocellulosic biomass, Bioresource Technology, 104, 687-694.

Gargiulo V., Alfe M., Giudicianni P., Ragucci R., 2016, A study on the structural features of the water-insoluble fraction (WIF) isolated from biomass slow steam pyrolysis liquids, Journal of Analytical and Applied Pyrolysis, 12, 128-137.

Gargiulo V., Giudicianni P. Alfe M., Ragucci R., Ferreiro A.I., Rabaçal M., Costa M., 2018, Experimental investigation on the effect of K+ ions on the slow pyrolysis of xylan, Chemical Engineering Transactions, 65, 553-558.

Gargiulo V., Giudicianni P. Alfe M., Ragucci R., 2019, About the Influence of Doping Approach on the Potassium Catalyzed Slow Pyrolysis of Xylan, Journal of Chemistry,2019, 1-11.

Guo D.L., Wu S.B., Liu B., Yin X.L., Yang Q., 2012, Catalytic effects of NaOH and Na2CO3 additives on alkali lignin pyrolysis and gasification, Applied Energy, 95, 22-30.

Jakab E., Faix O., Till F., Székely T., 1993, The effect of cations on the thermal decomposition of lignins, Journal of analytical and applied pyrolysis, 25, 185-194.

Jakab E., Faix O., Till F., 1997, Thermal decomposition of milled wood lignins studied by thermogravimetry mass spectrometry, Journal of Analytical and Applied Pyrolysis, 40, 171-186.

Patwardhan P.R., Satrio J.A., Brown R.C., 2010, Influence of inorganic salts on the primary pyrolysis products of cellulose, Bioresource Technololgy, 101, 4646-4655.

Phyllis2, Energy research Centre of the Netherlands, database for biomass and waste https://www.ecn.nl/phyllis2, accessed 10.12.2019.

Energy research Centre of the Netherlands Phyllis2, database for biomass and waste https://www.ecn.nl/phyllis2.

Tortosa Masiá A.A., Buhre B.J.P., Gupta R.P., Wall T.F., 2007, Characterizing ash of biomass and waste, Fuel Processing Technology, 88, 1071-1081.

Trubetskaya A., Timko M.T., Umeki K., 2020, Prediction of fast pyrolysis products yields using lignocellulosic compounds and ash contents, Applied Energy, 257, 113897.

Van Lith S.C., Jensen P.A., Frandsen F.J., Glarborg P., 2008, Release to the gas phase of inorganic elements during wood combustion. Part 2: Influence of fuel composition, Energy and Fuels, 22, 1598-1609.

Wang S., Ru B., Lin H., Sun W., Luo Z., 2015, Pyrolysis behaviors of four lignin polymers isolated from the same pine wood. Bioresource Technology, 182, 120-127.