



## Impact of organically bonded potassium on torrefaction: Part 1. Experimental



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### HIGHLIGHTS

- K, Na and to some extent Mn affect the mass loss during the torrefaction.
- Ca affects neither the mass loss nor the reaction rate in the course of torrefaction.
- The mass loss mainly depends on the K content rather than the biomass type.

### ARTICLE INFO

#### Article history:

Received 2 March 2015

Received in revised form 2 June 2015

Accepted 3 June 2015

Available online 13 June 2015

#### Keywords:

Torrefaction  
Alkali metal  
Calcium  
Doping  
Biomass  
TGA

### ABSTRACT

Torrefaction is a promising heat-treatment method being developed for biomass to increase the use of biomass in its thermochemical conversion processes. This type of pre-treatment can improve the properties of biomass for thermal conversion by improving grindability, heating value, reducing the hydrophilic nature, and increasing its resistance to biodegradation. In this work, we studied the impact of organically bound K, Na, Ca and Mn on mass loss of biomass during torrefaction. These elements were of interest because they have been shown to be catalytically active in solid fuels during pyrolysis and/or gasification.

In this work, we studied spruce and pine as coniferous woods, aspen as a deciduous wood and miscanthus as an herbaceous biomass. The biomasses were first acid washed to remove the ash-forming elements and then organic sites were doped with K, Na, Ca or Mn. The doping was performed in a nitrate solution of each metal. The resultant fuels were then torrefied at fixed temperatures between 240 and 280 °C in a thermogravimetric analyzer.

The results show that K and Na bound to organic sites can significantly increase the mass loss during torrefaction at temperatures between 240 and 280 °C for a fixed time and temperature. It is also seen that Mn bound to organic sites increases the mass loss while Ca addition does not influence the mass loss rate during torrefaction. This increase in mass loss during torrefaction with alkali addition is unlike what has been found in the case of pyrolysis where alkali addition resulted in a reduced mass loss. These results are important for the future operation of torrefaction plants which will likely be designed to handle various biomasses with significantly different contents of K. The results imply that shorter retention times are possible for high K-containing biomasses.

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### 1. Introduction

Torrefaction is a promising heat-pretreatment which can address some of the limitations of raw biomass for combustion and gasification. At the right conditions, this type of pretreatment can improve the grindability, reduce the hydrophilic nature of biomass; increase the heating value; and improve resistance to biodegradation [1].

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Raw biomass intrinsically contains different amounts of alkali and alkaline earth metals depending on the species, the fraction of the biomass and the soil. The different fractions of biomass, such as the different parts of a tree, can contain significantly different amounts of metals [2]. These metals affect the pyrolysis, gasification and combustion process (ex. [3–5]) by catalytically influencing the decomposition and char conversion mechanisms. The alkali and alkaline earth metals behave somewhat differently, both during pyrolysis and gasification [6,7]. For instance, the addition of K increases the char yield after pyrolysis [3]; whereas Ca usually affects the temperature of the maximum degradation rate during pyrolysis [8].

Several studies have been carried out on the catalytic effect of metals during the pyrolysis of biomass [6,8,9]. The presence of alkali metals affects the char yield as well as the ratio of the condensable to non-condensable volatiles [6]. It is apparent that a significant amount of information is known about the pyrolysis process, but there is very little information on the effect of metals on torrefaction.

Saddawi et al. [10] observed that when the key catalytic metal, particularly potassium, is removed from straw by water-washing for 24 h, the total amount of volatiles in the proximate analysis of washed straw torrefied at 290 °C was higher than the original straw torrefied at 290 °C. The influence of biomass impregnation by potassium carbonate and potassium chloride on torrefaction for 90 min at 270 and 300 °C showed that increasing the K content in biomass results in higher mass loss in course of torrefaction [11]. And, the presence of 2 wt.% KCl, has been shown to result in more CO, CO<sub>2</sub> and H<sub>2</sub>O during the pyrolysis of xylan and cellulose, even below 300 °C [12].

To probe the effect of metals on torrefaction, the samples were demineralized and then the selected metal was introduced. A common demineralization method is to remove metals with 2 M acid for 48 h at 60 °C [13–15]. However, due to the harsh effect of acid washing, some organics are also removed from the biomass. This is particularly true for hemicellulose, and the crystallinity of the cellulose can also be mildly affected [16]. To avoid the harsh effect of demineralization, Aho et al. [6] reduced the contact time to 1 h; and observed that most of the minerals were removed without appreciable hemicellulose degradation based on sugar analysis.

The common methods for loading cations into biomass in order to study their effect are: dry-mixing (adding dry salt to the biomass); impregnation (soaking the biomass in the salt solution and evaporating the solution) and doping or ion-exchange with protons on carboxylic and phenolic sites (soaking the biomass in a salt solution while adjusting the pH by the addition of a salt hydroxide in order to obtain the desired metal content, and finally, wash the biomass so as to remove any remained salts in the biomass matrix). Both dry-mixing and impregnation introduce the metal compounds to the biomass as an inorganic salt; however, ion-exchange bonds the cation to the organics.

In this work, we have studied the catalytic effect of alkali metals with a focus on the effect of potassium on biomass torrefaction. We studied spruce and pine as coniferous species; aspen as a deciduous wood and miscanthus as a herbaceous biomass. The alkali metals were removed from the sample by acid washing and then K, Na, Ca or Mn was added selectively to the functional groups of the biomass sample. Potassium was also added as K<sub>2</sub>CO<sub>3</sub> by impregnation to determine if it behaved similarly to the K doped to organic sites. To investigate the effect of the metals on biomass components, galactoglucomannan, cellulose and lignin derived from spruce wood were impregnated with K<sub>2</sub>CO<sub>3</sub> and then torrefied. Torrefaction was carried out in a Thermo Gravimetric Analyzer (TGA). Torrefaction temperatures were between 240 and 280 °C. The concentration of some of the ions was varied to obtain the impact of concentration.

## 2. Experiments

### 2.1. Preparing samples

*Origin:* The samples used in this work were three woody biomasses, the coniferous woods spruce and pine; and aspen was studied as a deciduous wood. Miscanthus was used as a herbaceous biomass. In addition to these biomass components, galactoglucomannan, cellulose and lignin were used. Galactoglucomannan, crystalline cellulose and lignin were isolated

from spruce wood while Whatman ash-free filter paper was used as the cellulose sample for torrefaction at 280 °C.

The biomasses were ground and sieved and then the fraction between the 125 and 250 µm sieves was used. Before torrefying the samples, some of them were acid-washed, and then loaded with selected metals either by ion-exchange or impregnation. Table 1 shows the investigated conditions.

*Washing to remove metals:* The biomass samples were prepared by washing with a two-step process utilized earlier by Khazraie Shoulaifar et al. [17]. First the biomass was added to a 0.01 M sodium EDTA containing aqueous solution for 2 h at room temperature. The washed sample was then rinsed with water and then washed with 0.01 M HCl for 2 h. Finally the samples were rinsed with ultra pure water. After acid-washing, the elements K, Mn and Na were below the detection limit of ICP analysis and the analyzed concentration of Ca was less than 5%, Table 3. The acid-washed wood was then oven-dried at 105 °C overnight.

*Doping:* The acid-washed biomass was doped with K, Na, Ca or Mn by adding 1.5 g of dried biomass to a 50 ml of the 0.05 M metal nitrate solution for 24 h. The pH of the solution was adjusted to 5, 8 or 12 by the addition of the metal hydroxide. The suspension was filtered and the biomass was washed with ultrapure water. The biomass was then dried overnight in the oven at 105 °C.

*Impregnation:* Three grams of dried acid-washed spruce was impregnated in 50 mL of 0.003 M potassium carbonate aqueous solution. The suspension was stirred for 60 min, and then, the aqueous solution was filtered. The impregnated sample was then dried overnight in the oven at 105 °C.

Impregnation of hemicellulose, cellulose and lignin was performed by mixing 1 g of dried material in 50 mL of an aqueous solution containing 0.003 M K<sub>2</sub>CO<sub>3</sub> for 60 min. The solution was placed in a freeze-drier and the dried cellulose/hemicellulose was kept in a desiccator before using. Freeze-drying was used instead of oven-drying for the biomass components because the final dried component was fluffier and could be easily ground. If all of the K<sub>2</sub>CO<sub>3</sub> in the solution was absorbed onto the wood components, the K resulting concentration would be 1.16 wt.%. The metal contents of the untreated and treated biomass components were analyzed by burning the samples in a TGA at 540 °C for 60 min and the weight was measured. This can be converted to K by assuming the ash is 100% K<sub>2</sub>CO<sub>3</sub>. Burning the untreated hemicellulose, cellulose and lignin resulted in no ash after combustion, while burning the impregnated components of biomass gave a concentration of 1.2 wt.% K which is consistent with the calculated 1.16 wt.% K.

### 2.2. Torrefaction

The weight yield during torrefaction was analyzed in a Thermo Gravimetric Analyzer (TGA), TA Instruments Q600. The biomass (8–12 mg) was loaded in an Al<sub>2</sub>O<sub>3</sub> cup for torrefaction and then inserted into the TGA furnace. The sample was heated at a rate of 20 °C/min up to the torrefaction temperature (240–280 °C) and held at that temperature isothermally for 30 min. Nitrogen was purged as a carrier gas into the TGA at a flow rate of 100 N mL/min to avoid any oxidation reaction during the experiments. The temperatures of torrefaction run for various biomass feedstock are shown in Table 1. In order to be sure that the moisture content inside the biomass did not affect the final mass yield, a few replicates were made in which the sample was held at 150 °C, for 10 min prior to heating to the torrefaction temperature, and no difference was observed. The mass losses after torrefaction are shown in Appendix A. In addition to the torrefaction experiments, some pyrolysis experiments were run in the TGA. A heating rate of 20 °C/min with a 100 mL/min nitrogen flow was used. The final temperature of the pyrolysis experiments was 800 °C.

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