



Research article

Influence of potassium carbonate addition on the condensable species released during wood torrefaction



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ABSTRACT

In order to investigate the effect of potassium addition on the composition of torrefaction condensates, two demineralized wood species were impregnated with different concentrations of K_2CO_3 and then torrefied at 275 °C up to an anhydrous weight loss (AWL) of 25%. Torrefaction was carried out in both a thermogravimetric analysis (TGA) instrument and a laboratory fixed-bed reactor. Condensates from the fixed bed reactor were collected and analyzed by Gas Chromatography-Mass Spectroscopy (GC-MS). TGA of raw and K_2CO_3 -impregnated biopolymers (cellulose, xylan and lignin) were performed to facilitate interpretation of the results. TGA showed that when potassium content increased in the biomass, shorter torrefaction times were sufficient to obtain the targeted AWL. GC-MS showed, for both wood species, that potassium promotes the formation of acetol and slightly enhances acetic acid yield. The amount of some lignin derivatives (guaiacol, syringol, 4-vinylguaiacol) also rose with potassium addition. Yields of levoglucosan, LAC (1-hydroxy-(1R)-3,6-dioxabicyclo [3.2.1]octan-2-one) and DGP (1,4:3,6-dianhydro- α -D-glucopyranose), as well as furfural and 5-hydroxymethylfurfural, decreased drastically in the presence of potassium. In conclusion, small additions of potassium carbonate deeply affected thermal degradation of wood species and the speciation of torrefaction condensates.

1. Introduction

Torrefaction is a mild pyrolysis process usually carried out between 200 and 300 °C in the absence of oxygen, and is used to increase the hydrophobicity, energy content and grindability of biomass [1]. Torrefaction, which is regarded as a biomass pretreatment method, has been studied for gasification [2–5] and combustion applications [6–8]. In a conventional torrefaction process, the solid product amounts to about 70% of the initial dry weight of the biomass and the remainder is released as condensable and non-condensable gases [9], which are still under-exploited. Recent studies have suggested that condensable gas could be potentially utilized as bio-sourced chemicals [10,11] and should be considered for enhancing economic viability in torrefaction plants. Efforts have been made to identify and quantify condensable species released during biomass torrefaction and more than 85 condensable products have been reported, in addition to discovering the strong influence of temperature and biomass composition in their

formation [11].

During thermal degradation, mineral matter may affect the behavior of biomass components, altering the distribution and chemical speciation of the pyrolysis products. The mineral matter content of raw biomass may vary from less than 1 wt% to more than 25 wt% depending on the type of biomass, mainly consisting of Al, Ca, Fe, K, Mg, Na and Si, with smaller amounts of S, P, Cl and Mn [12]. Among the metals present in biomass, potassium appears to have the greatest influence on thermal degradation mechanisms [13] and generally its content in biomass is much higher than other alkali metals [14]. The influence of alkali metals on biomass pyrolysis has been widely studied and the catalytic role of potassium in char formation at the expense of pyrolysis liquid yield has been reported [15–17]. Contrary to what occurs under pyrolysis temperatures, an increasing mass loss with potassium addition has been observed during torrefaction, which might allow the use of shorter residence times as well as lower temperatures to obtain the target solid yield [18,19]. These torrefaction studies, however, did not

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analyze the effect of potassium addition on the composition and yield of the condensable species.

Increasing potassium content may enhance lignin derivative yield during pyrolysis [20,21]. Some of these pyrolytic compounds, such as guaiacol, vinyl-guaiacol, syringol, syringaldehyde, eugenol, isoeugenol and vanillin are recognized as valuable chemicals and could be considered for future biorefinery approaches. Hence, understanding the catalytic effect of potassium during biomass torrefaction may be an important step towards chemical utilization of condensable gases in future torrefaction plants, in addition to torrefied biomass.

Consequently, to analyze the influence of potassium content on condensable species released during wood torrefaction, two demineralized wood species were impregnated with three different concentrations of K_2CO_3 and then torrefied at 275 °C up to an anhydrous weight loss (AWL) of 25%. In order to gain a better understanding of the role of potassium in thermal degradation, cellulose, lignin and xylan (representing hemicelluloses) were also impregnated with K_2CO_3 and studied by thermogravimetric analysis (TGA). Torrefaction of the wood species was carried out in both a TGA instrument and a laboratory-scale fixed-bed reactor. Condensates from the fixed-bed reactor were collected and analyzed by GC–MS.

2. Material and methods

2.1. Biomass feedstock and sample preparation

The woody biomass consisted of a eucalyptus hybrid clone (*Eucalyptus urophylla* x *E. camaldulensis*) and amapaí (*Brosimum potabile* Ducke), a tropical wood species. Biomass was knife-milled down to a particle size of < 1 mm and then dried for 24 h at 105 °C in a forced-draft oven prior to demineralization, impregnation and torrefaction experiments. Microcrystalline cellulose (Avicel PH105; 20 µm; product code 14205) and xylan from beech wood (product code 38500) were purchased from Serva Electrophoresis. Lignin kraft (product code 370959) was purchased from Sigma Aldrich. The biomass components were dried as received and they were not demineralized prior to impregnation and TGA.

2.2. Demineralization and impregnation of samples

Wood samples were washed with 1% acetic acid (Sigma Aldrich, purity 99.7%) in accordance with the procedure used by Wigley et al. [22]. We decided to work with an organic acid instead of the mineral acids usually employed, to avoid major modifications in biomass polymer composition induced by acid leaching, and to gain a better understanding of the effects of mineral matter removal and potassium addition. First, 50 g of dried wood was added to 500 mL of leaching solution using a 1 L beaker glass. The beaker was then heated to 30 °C for 4 h using magnetic hotplates with a stirring speed of 250 rpm. Lastly, the samples were rinsed with deionized water in a vacuum using a Buchner funnel with filter paper (Rundfilter MN615, Macherey-Nagel). The acid-washed samples were then oven-dried for 24 h at 105 °C.

Even though the chosen acid-washing method does not change significantly the polymer composition of wood samples, it was not employed for isolated polymers (cellulose, xylan and lignin). These polymers, when arranged together in the wood fiber structure, are expected to be more resistant to changes induced by acid leaching than their isolated form. For instance, the presence of xylan-lignin and xylan-cellulose bonds may impact xylan hydrolysis [23]. In this same sense, the amount of hydroxyl groups in isolated lignin may be reduced by acid washing [24].

Demineralized wood samples were impregnated with three different concentrations of K_2CO_3 (Sigma Aldrich, purity 99.99%) based on the procedure employed by Shoulaifar, et al. [18]. Thirty grams of oven-dried woody samples was immersed in 1 L of 0.003 M, 0.006 M and

Table 1

K, Na, P and Ca content in control, raw and impregnated biomass analyzed by ICP-AES. *DL: detection limit.

wt%, dry basis	K	Na	P	Ca
Eucalyptus				
Control	0.009	0.005	0.0028	< DL*
Raw	0.027	0.012	0.0030	< DL
0.003 M K_2CO_3	0.149	0.003	0.0065	< DL
0.006 M K_2CO_3	0.253	0.004	< 0.0028	< DL
0.009 M K_2CO_3	0.387	0.004	0.0095	< DL
Amapaí				
Control	0.011	0.005	0.0081	0.008
Raw	0.086	0.026	0.0140	0.179
0.003 M K_2CO_3	0.229	0.004	0.0099	0.054
0.006 M K_2CO_3	0.314	0.004	0.0050	< DL
0.009 M K_2CO_3	0.527	0.006	0.0091	0.005
Cellulose				
Raw	0.018	0.004	0.0046	< DL
0.003 M K_2CO_3	0.096	0.008	< 0.0028	< DL
Lignin				
Raw	0.114	0.531	< 0.0028	< DL
0.003 M K_2CO_3	0.230	0.186	0.003	< DL
Xylan				
Raw	0.223	1.043	0.0132	0.600
0.003 M K_2CO_3	0.614	1.080	0.0142	0.634

0.009 M K_2CO_3 aqueous solution. Cellulose, lignin and xylan were impregnated in the 0.003 M K_2CO_3 solution only. The suspension was stirred at 250 rpm for 60 min, and then filtered through a filter paper (Rundfilter MN615, Macherey-Nagel) in a Buchner funnel. Given the difficulty of filtering the suspension of xylan in water, freeze drying was used instead of filtration and consequently all of the K_2CO_3 in the solution was retained in xylan, and thus, the K content was higher than that observed in the cellulose and lignin samples. The impregnated samples were then oven dried for 24 h at 105 °C.

These samples were labeled according to the K_2CO_3 concentration of the impregnation solution in which they were immersed (0.003 M K_2CO_3 , 0.006 M K_2CO_3 and 0.009 M K_2CO_3). Demineralized samples without addition of salt served as the control. After demineralization and impregnation, the samples were analyzed for inorganic elements by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) (Table 1). The K content of the samples varied from 0.009 to 0.614 wt %, corresponding to the range in which the effect of K in torrefaction mass loss is more pronounced [18].

2.3. Thermogravimetric analysis (TGA)

The behavior of raw, control and potassium-impregnated biomass samples was studied under an inert nitrogen atmosphere in a thermogravimetric analyzer. A constant flow rate of 0.5 L/min was applied. Each of the biomass samples (100 ± 15 mg) in an alumina pan was heated up from room temperature to 105 °C and kept isothermally at that temperature for 30 min to remove the moisture. The samples were then heated to 275 °C with a heating rate of 10 °C/min and held at that temperature isothermally for 50 min. All the TGA experiments were replicated twice. The repeatability of the TGA experiments was good, with a relative standard deviation between two replications of less than 1%.

2.4. Torrefaction experiments

The fixed-bed reactor consisted of an external stainless steel tube (500 mm high, 36 mm ID) and an internal quartz tube reactor (410 mm high, 26 mm ID), equipped with a fixed porous bed on the top to hold the biomass. The external tube was closed at the top and heated by a 4 kW furnace. A constant N_2 flow rate of 0.55 L/min was applied. The

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