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Effects of Potassium on the Decomposition of Wood and Lignocellulosic Components During Torrefaction

Larissa Richa[1*], Baptiste Colin[1], Anélie Pétrissans[1], Rafael L. Quirino[2], Wei-Hsin Chen[3,4,5], Mathieu Pétrissans[1]

1 Université de Lorraine, INRAE, LERMaB, F-88000 Epinal, France
2 Chemistry Department, Georgia Southern University, Statesboro, GA-30460, USA
3 Department of Aeronautics and Astronautics, National Cheng Kung University, Tainan, 701, Taiwan
4 Research Center for Smart Sustainable Circular Economy, Tunghai University, Taichung 407, Taiwan
5 Department of Mechanical Engineering, National Chin-Yi University of Technology, Taichung 411, Taiwan
*Corresponding author: Email: larissa.richa@univ-lorraine.fr

ABSTRACT

Potassium (K) is among the most abundant minerals in plants and is responsible for their growth. It has a major role on the degradation of lignocellulosic biomass. However, there are some questions about the behavior of potassium during torrefaction. To fully understand the role of this mineral in torrefaction, a thermogravimetric analysis was performed on beech wood and its components: cellulose, hemicelluloses and lignin. The samples were impregnated with different potassium carbonate K_2CO_3 concentrations (0.004 M, 0.008 M, and 0.012 M). The results showed that the effect potassium depends on the temperature and the residence time. The TG curves of wood with different potassium concentrations intersected at the same mass loss percentage. After the intersection point, K switched from degrading the biomass to favoring char formation. The potassium was found to act mostly on cellulose and hemicelluloses. After carbohydrate degradation, the relative lignin content increases, which could potentially be the reason behind the increased char production with potassium. The obtained results provide a novel insight on the role of potassium in thermal treatment of biomass. This information could be conductive to a reduction of the process time and/or temperature, thus rendering the torrefaction an advantageous pretreatment for wood used for combustion.

Keywords: Potassium catalyst, Inhibitor, Torrefaction, Polymers degradation, Combustion.

1. INTRODUCTION

Given the exponential growth of the population and the development of industries, energy demand is also increasing. Consequently, renewable energies, such as hydropower, wind, solar, and biomass are investigated in order to reduce the negative impact on the atmosphere due to the use of conventional fuel sources [1]. Favoring wood over fossil fuel in effectively reduces the CO_2 emissions and could tackle the global warming [2].

Torrefaction of biomass is a thermal treatment at 200-300°C in an inert atmosphere. It can effectively upgrade biomass and improve the quality of solid biofuel (biochar). This preconditioning treatment leads to lower moisture content and atomic O/C and H/C ratios. Moreover, it results in a higher heating value of the biomass and a better grindability that increase the energetic yield of combustion. Biomass decomposition during torrefaction and pyrolysis mainly depends on its three polymer constituents: hemicelluloses, cellulose and lignin. The minerals present in wood impact the mechanisms of degradation as well [3]. Among which is the potassium present in the wood in its ionic form (K^+), mobile or attached to some functional groups, or as dissolved salts [4]. When wood is dried, the cationic potassium probably links to form salts including KCl, K_2SO_4, KOH, and K_2CO_3 [5]. It is valorized in combustion as it increases the decomposition rate. It causes a heterotic ring fission and cracking reactions thus favoring the formation of low molecular weight components and char over levoglucosan and furans [6]. The potassium remains in the char and is a catalyst for combustion that

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increases the conversion in terms of carbon burn-out [7]. Nonetheless, few studies have been conducted on the role of potassium in torrefaction as a pretreatment for combustion.

The aim of this study is to obtain a better understanding on the impact of K on the torrefaction of wood and its separate components. It investigates the influence of time and temperature on this impact.

2. MATERIALS AND METHODS

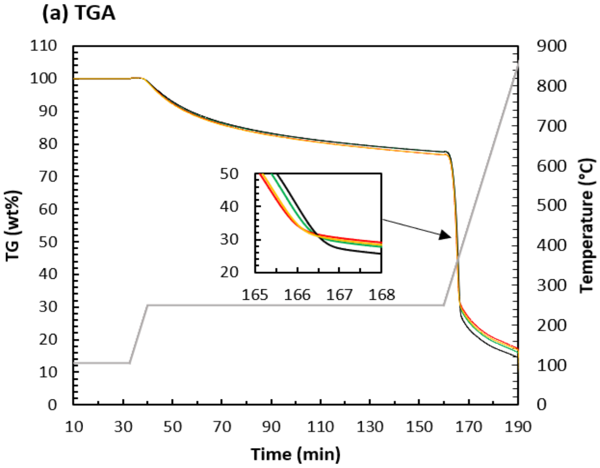
2.1 Sample preparation

Beech wood (*Fagus sylvatica*) was used in this present work due to its abundance and limited use in the French market. Filter paper (*Whatman Ashless, d= 42.5mm*) was used as cellulose. It is composed of high purity α-cellulose (>99%) and is used in literature [8-9]. Beech xylan (*Sigma Aldrich*) was chosen to represent the hemicelluloses present in beech. Lignin was extracted from an American paper mill (*Domtar*).

The biomass was enriched with potassium through the chemical impregnation with K_2CO_3, following a procedure widely adopted in literature [8-10-11]. Potassium carbonate K_2CO_3 (*Sigma Aldrich*), was obtained with 99.99% purity. By comparing different salts, carbonate was found to has the least effect on the torrefaction [6]. As consequence the dominant impact observed is that of K. The potassium solutions were prepared according to the desired K_2CO_3 concentrations (0.004M, 0.008M and 0.012M) by dissolving with deionized water.

The impregnated materials were beech wood, cellulose, beech xylan and lignin. The samples were ground with a knife-mill SM100 (*Fritsch, Germany*) equipped with trapezoidal meshes of 0.5 mm and dried for 24 h at 60°C. The impregnation was done using 2g of the dry sample mixed with a mixing ratio of 10 mL g^{-1} of K_2CO_3 solution at ambient conditions. The mixture was stirred for 1 h before vacuum filtration (*Büchner*). The retained solid was finally dried for 24 h at 60°C. Xylan could not be

(a) TGA



(b) DTG

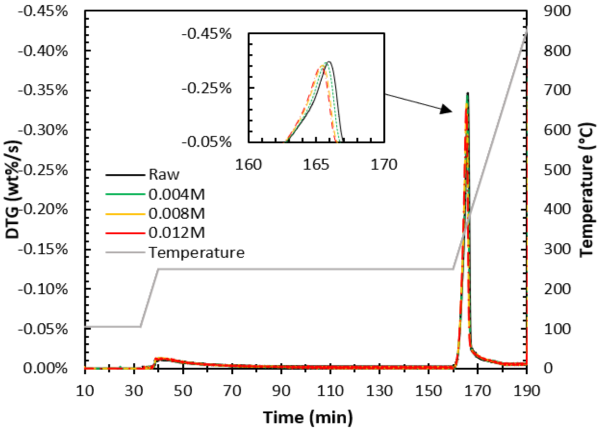
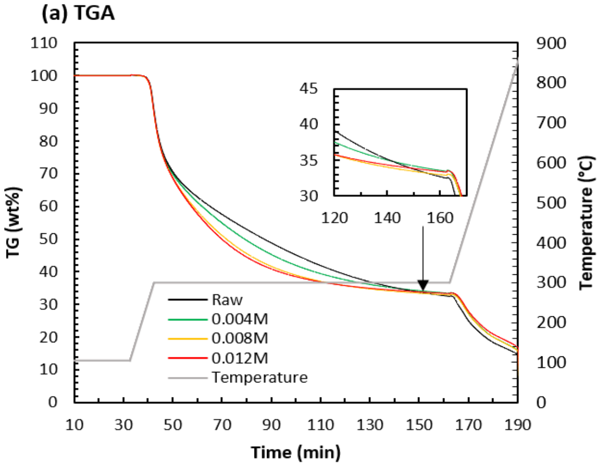


Fig. 1. TG (a) and DTG (b) of beech torrefaction at 250°C for different potassium concentrations

(a) TGA



(b) DTG

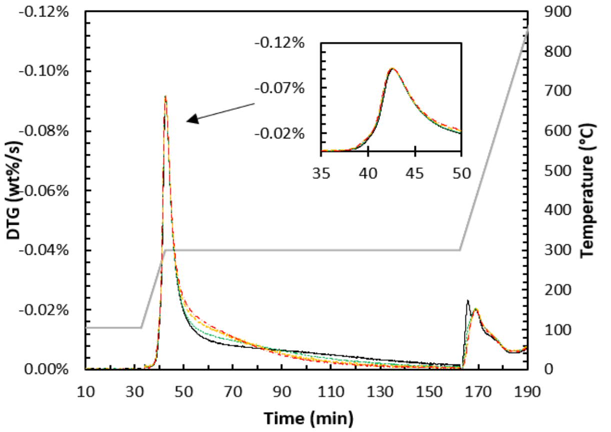


Fig. 2. TG (a) and DTG (b) of beech torrefaction at 300°C for different potassium concentrations

filtered and was directly dried in the oven after impregnation.

2.2 Thermogravimetric analysis

The degradation of wood during the torrefaction and pyrolysis was assessed by means of a thermogravimetric analysis (TGA). It relies on a precise thermal balance that registers the decrease of sample weight as a function of time and temperature. The thermal balance *Mettler Toledo TGA-2* was run under inert atmosphere using 100mL min^{-1} of N_2. Powdered samples were dried at 105°C for 24h prior to the experiments. The biomass (5mg) was loaded in the crucible where it was heated from 50°C until 105°C at a heating rate of 20K min^{-1}. The system was held at this temperature for 30 minutes for moisture removal. Then, it was heated to the desired torrefaction temperature (250°C, 300°C or 380°C) and kept isothermal for 2h. The isothermal step is useful to understand the change in kinetics due to the potassium. The sample was then pyrolyzed until 850°C with the same heating rate of 20K min^{-1}. The DTG was obtained as the derivative of each point of the TGA curve. To ensure the repeatability of the results, all TGA were duplicated and the obtained difference was less than 2wt%.

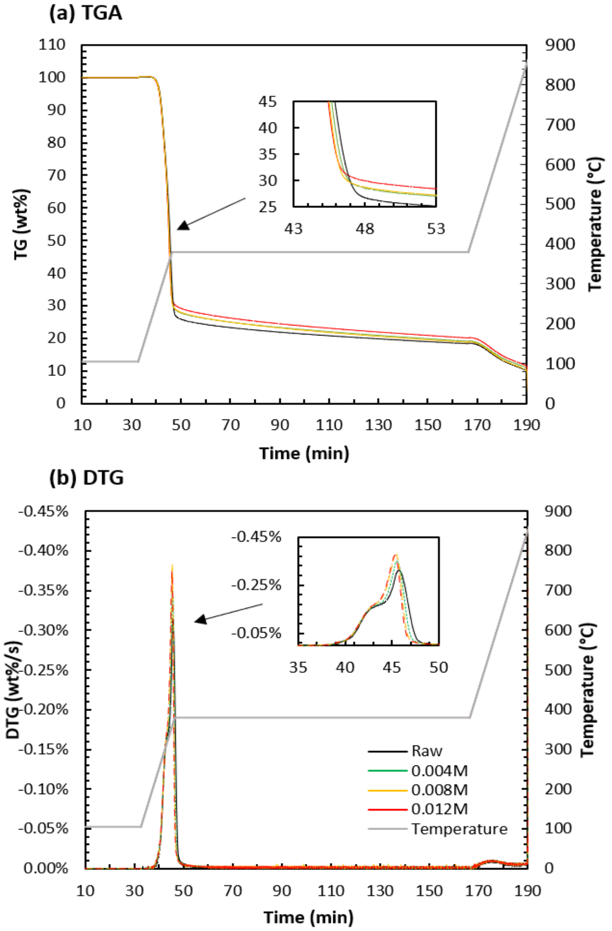


Fig. 3. TG (a) and DTG (b) of beech torrefaction at 380°C for different potassium concentrations

3. RESULTS AND DISCUSSION

The TG and DTG results for each of the selected torrefaction temperatures are shown in **fig.1-3.** The potassium significantly impacted the kinetics at the isothermal step at 300°C (**fig.2**). At 82 minutes, the weight was 8.47% lower when K increased from raw to 0.012M. At the end of the torrefaction, the curves intersected at the same mass loss (34wt%), after which K switched from catalyzing the degradation of wood to favoring char formation. This behavior was detected by Yang et al. [11] stating that at temperatures below 315°C the potassium acts as a catalyst while at higher temperatures, the increase of K leads to more char. However, the results obtained in this study showed that the effect does not depend on temperature solely but on the torrefaction time as well.

Although the effect of the potassium at 250°C (**fig.1**) was not important, it was observed that it slightly catalyzed the degradation reactions of the biomass

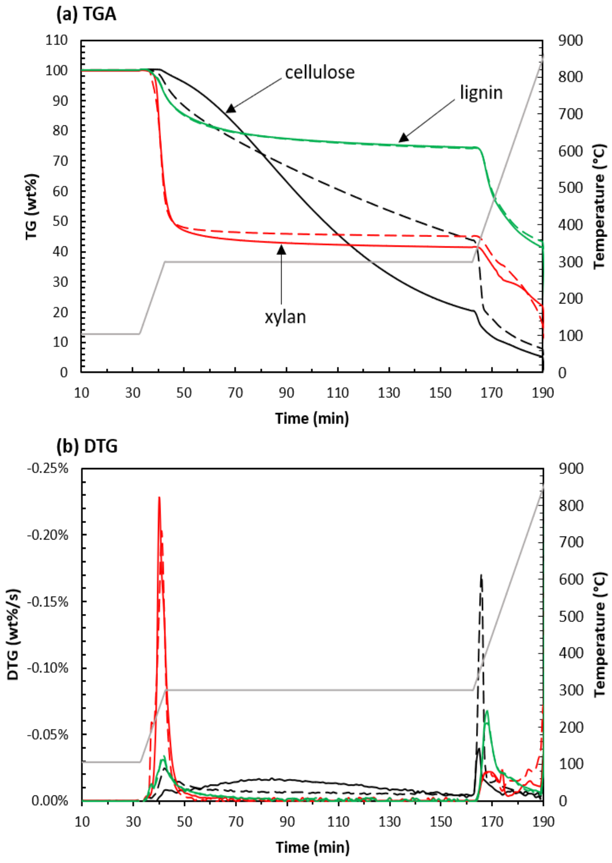


Fig. 4. TG (a) and DTG (b) of torrefaction of the individual components at 300°C. The dashed curves correspond to the samples impregnated with 0.004M of K_2CO_3

during the isothermal plate. This trend was inverted during the pyrolysis stage at 380°C. Thus, clearly demonstrating the double role of K on the torrefaction/pyrolysis. The promoted char formation occurred as well during the torrefaction at 380°C (**fig.3**). At the beginning of the isothermal plate the char yield increased by 3.3wt% for beech with 0.012M of K compared to raw sample, due to polycondensation [10].

Moreover, for each torrefaction temperature, the curves intersected at the same point (32-35wt% left). At these conditions, most of the hemicelluloses and cellulose are decomposed, leaving a relatively high lignin content [10]. It is speculated that the role of K depends on the composition of the wood. After a certain threshold of lignin content, there is inhibition of thermal degradation in the presence of K. It is possible that when lignin becomes the dominant component in the sample, lignin-K interactions favor deoxygenation reactions, promoting the formation of highly aromatic products (char). This is consistent with the research of Saleh SB et al. highlighting that the torrefaction produced more char with the addition of K, for the wood that was rich in lignin (36.8wt% db) [12]. This hypothesis contradicts the study of Xing et al. [13] where potassium inhibited the decomposition of hemicelluloses and promoted the degradation of both cellulose and lignin.

The TGA of the individual components of wood (**fig.4**) showed that the presence of K impacted the cellulose and hemicelluloses. The DTG of cellulose showed that the temperature of max degradation shifted to a lower temperature similar to that of hemicelluloses at around 280°C, which is consistent with literature [11]. The impregnation with 0.004M of K increased the char yield of xylan at 300°C. While both TGA and DTG of lignin showed no differences with impregnation.

4. CONCLUSIONS

The effect of potassium on the torrefaction of wood was studied. This process is used as a preconditioning for combustion. The experiments showed that K had an effect on the thermal degradation of wood. It had a more prominent role at 300°C, acting as a catalyst by rapidly decreasing the mass of the sample. However, after 34% mass left, it promoted the char formation. K reduced the temperature of max degradation of cellulose. It also acted on hemicelluloses by leading to more char formation. However, lignin remained difficult to degrade and was not impacted by the presence of K. By understanding the impact on the individual components, a systematic relationship to the whole biomass will be possible. Potassium impregnation could be a solution to enhance the properties of biomass that facilitate the grinding and reduce the operating cost.

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