Role of potassium impregnation on the interactions of lignocellulosic components of biomass during torrefaction

RICHA Larissa[1], COLIN Baptiste[1], PETRISSANS Anélie[1], L. QUIRINO Rafael[2], CHEN Wei-Hsin[3], PETRISSANS Mathieu[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
larissa.richa@univ-lorraine.fr

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Introduction

Biomass has gained importance in the renewable energy field. It produces biofuels that can generate heat and power and could be used in transportation. However, some treatments such as torrefaction are required to improve its physical and mechanical properties (Chen et al., 2021). Lignocellulosic biomass is composed of three main compounds cellulose, hemicelluloses and lignin. From a chemical perspective, hydrogen bonding exists between the cellulose and lignin, as well as the cellulose and hemicellulose. Additionally, covalent linkages, mainly ether bonds, have been proposed to be present between cellulose and lignin (Jin et al., 2006). Multiple studies have been conducted to understand these interactions in wood, however, they reached different conclusions. For instance, Zhang et al. (2015) found negligible interactions for binary physical mixtures and for the native cellulose−hemicellulose mixture. In the case of the native cellulose−lignin mixture, herbaceous biomass exhibited an apparent interaction. However, such an interaction was not found for woody biomass. It is speculated that these results are due to different amounts of covalent linkages in these biomass samples (Zhang et al., 2015). In contrast others state that the interactions between the polymers and between the intermediate products greatly impact the kinetics of the thermal degradation of biomass. Therefore, the superposition of these components is not sufficient to represent wood (George et al., 2014; Hosoya et al., 2007). Potassium (K) is a mineral present in plants that has a catalytic role on biomass torrefaction. It is speculated that K cleaves the hydrogen bonds and glycosidic linkages in cellulose and promotes the char formation of hemicelluloses (Khazraie Shoulaifar et al., 2016; Nishimura et al., 2009). The purpose of the present work is to understand the impact of the interactions of the lignocellulosic components on the wood torrefaction. Focusing on the role of potassium on these links and on the decomposition of the individual components and of native wood. Therefore, a thermogravimetric analysis (TGA) was performed on potassium impregnated samples of beech, cellulose, xylan and lignin. Then a simulated TG was obtained by superposition of these components and compared with the experimental data.

Materials and methods

Sample preparation

The biomass chosen for this work was beech wood (*Fagus sylvatica*) to possibly valorize it in the French market. Filter paper made of high purity α-cellulose (*Whatman Ashless*) was used as cellulose (Khazraie Shoulaifar et al., 2016; Nishimura et al., 2009). Hemicelluloses were represented by beech xylan (*Sigma Aldrich*). Lignin was obtained by extraction from an American paper mill (*Domtar*). The biomass was enriched with potassium through the chemical impregnation with potassium carbonate K_2CO_3 (*Sigma Aldrich, 99.99% purity*) (Khazraie

Shoulaifar et al., 2016; Safar et al., 2019). Potassium solutions were prepared by mixing with deionized water according to the desired K_2CO_3 concentrations (0.004M, 0.008M and 0.012M) and are labelled accordingly. The impregnated samples were beech wood, cellulose, beech xylan and lignin. They were ground and dried for 24 h at 60°C. Then 2g of the dry sample were mixed at ambient conditions with a mixing ratio of 10 mL g^{-1} of K_2CO_3 solution. The mixture was stirred for 1 h before vacuum filtration (*Büchner*). The retained solid was finally dried for 24 h at 60°C. Due to the difficulty in filtering, xylan was only dried in the oven after impregnation.

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. Then 5mg of the sample was introduced in the crucible and heated from 50°C until 105°C at a heating rate of 20K min^{-1}. It was held for 30 min this temperature to remove moisture. Then the sample was heated to the desired torrefaction temperature (300°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 a heating rate of 20K min^{-1}. The DTG was obtained as the derivative of each point of the TG curve as a function of time. The TGA experiments were duplicated to ensure the repeatability of the experiments. A difference of less than 2wt% was obtained between the TG curves of the two trials.

Calculation of simulated TG

Based on the composition of beech from literature (*Tab.1*), the addition of the separate components is calculated to check if the equivalent curve overlaps with the experimental TG of beech. In order to do so, a component mass balance was applied which consists of considering that the sum of the mass of the beech's constituents (lignin, xylan and cellulose) should represent the behavior of beech wood. Therefore, the following mass formula is applied for each mass obtained in the TG:

$$m_{simulated} = \sum x_i \times m_i$$

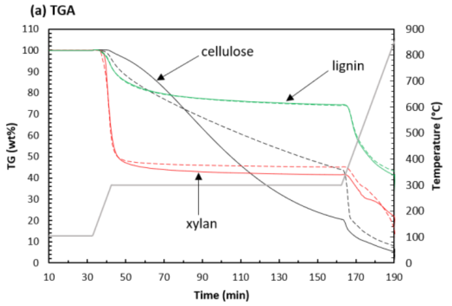
x_i is the mass fraction of component i (lignin, xylan or cellulose) with $0 \leq x \leq 1$, m_i is the mass percent of component *i* (in wt%) as obtained from the TGA.

Results and discussion

The TG curves in *fig.1* show that the degradation of cellulose was catalyzed and onset earlier by the addition of potassium. Moreover, it shifted temperature of max degradation (DTG peak) of cellulose to a lower one that matches that of xylan (Yang et al., 2006). This change is attributed to the change of crystalline cellulose into amorphous cellulose caused by potassium (Lin et al., 2021). As for xylan, the potassium increased the char formation during torrefaction and pyrolysis. Both the TG and DTG of lignin show no differences with impregnation which is logical since lignin is a complex molecule that is hard to degrade (Chen et al., 2021).

By adding the TG of each component according to their percentage in wood, the resulting simulated wood degradation is obtained (*fig. 2*). For raw samples, the simulated curve (red) does not overlap with the experimental (black) which is due to multiple factors. When extracting the components, the links between each other are broken (hydrogen and covalent bonds mostly). This difference shows that these interactions have an impact on torrefaction which opposes some sources in literature that found no obvious interactions at low temperatures (Yang et al., 2006; Yu et al., 2017). Also, the extractives were not accounted for in the summation, however they participate in the degradation of wood. They start to volatilize at low temperatures which explains why the experimental curve is below the simulated one (Khazraie Shoulaifar et al., 2016). Moreover, the addition of potassium seems to further increase the difference between the curves until 0.008M, after which, the difference decreases again. These results prove that potassium interacts with the separated components increasing the gap between measured and calculated curves.

(a) TGA



(b) DTG

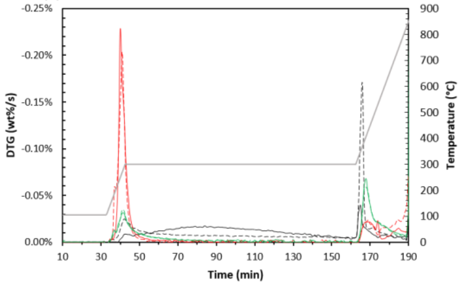


Fig. 1: TGA (a) and DTG (b) of lignocellulosic components torrefied at 300°C (continuous line is raw and dashed line is 0.004M)

Tab. 1: Beech wood composition from literature (Bodîrlău et al., 2008)

Component	**Mass percentage (wt%)**
Hemicelluloses	21.35
Cellulose	47.66
Lignin	25.53
Total	94.54

Conclusions

In order to understand the effect of potassium on the thermal degradation of wood, it is important to study the decomposition of its constituents as well. Therefore, beech wood and its separate components: α-cellulose, beech xylan and lignin were impregnated with K_2CO_3 and torrefied using TGA. As a conclusion, potassium impacts mostly the cellulose followed by xylan and has little effect on lignin.

Moreover, a simulated TG curve was sketched based on the addition of the TG of each component. The results show that potassium impacts the interactions between the components. It leads to a higher difference between the experimental degradation kinetics of beech and the simulated one. Therefore, as opposed to what some literature states, the interactions between the individual components of wood cannot be neglected during torrefaction. Therefore, the separate components do not behave the same way as in the native wood. Furthermore, potassium seems to break some of these links even at ambient conditions. Additional studies should be done to deeply understand this phenomenon, which could promote the use of potassium impregnation as a process for facilitating the torrefaction of wood.

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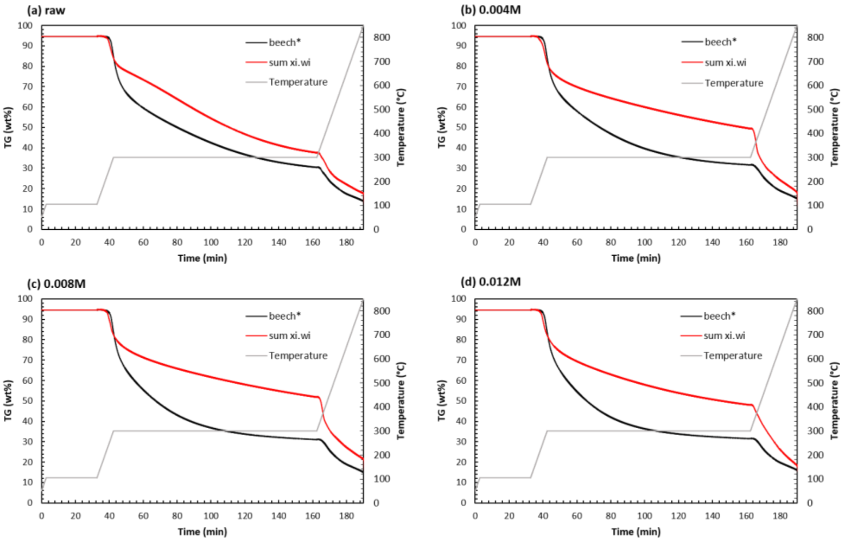

Fig. 2: TG curves of beech and the simulated addition of its components for different potassium concentrations: raw (a), 0.004M (b), 0.008M (c) and 0.012M (d)

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