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Catalytic and char-promoting effects of potassium on lignocellulosic biomass torrefaction and pyrolysis

Larissa Richa [a,*], Baptiste Colin [a], Anélie Pétrissans [a,*], Ciera Wallace [b], Allen Hulette [b], Rafael L. Quirino [b], Wei-Hsin Chen [c,d,e,**], Mathieu Pétrissans [a]

[a] Université de Lorraine, INRAE, LERMaB, F-88000 Epinal, France
[b] Chemistry Department, Georgia Southern University, Statesboro, GA 30460, USA
[c] Department of Aeronautics and Astronautics, National Cheng Kung University, Tainan, 701, Taiwan
[d] Research Center for Smart Sustainable Circular Economy, Tunghai University, Taichung 407, Taiwan
[e] Department of Mechanical Engineering, National Chin-Yi University of Technology, Taichung 411, Taiwan

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ABSTRACT

Torrefaction is a potential pretreatment method to produce biochar used as a solid fuel or as an environmentally friendly construction material. However, the torrefaction performance varies when wood composition and mineral content change. Potassium (K) is an abundant mineral present in plants and is claimed to influence the degradation of lignocellulosic biomass. Therefore, a full understanding of the role of potassium is required to predict torrefaction behavior. Samples of beech, celluloses, hemicelluloses, and lignin were impregnated with different potassium carbonate K_2CO_3 concentrations (0.004, 0.008, and 0.012 M). Thermogravimetric analysis was utilized to analyze their thermal degradation characteristics under different temperatures. At 250 °C, the catalytic effect of potassium was weak. At 300 °C, potassium acted as a catalyst until a precise mass loss (65 wt%) and torrefaction duration (105 min) promoted char formation. The changed effect of this weight loss was possibly related to the relative increase in lignin content compared to cellulose and hemicelluloses While at a higher temperature (380 °C), the catalytic effect of potassium was rapid, and the increased char content was better observed. The potassium was found to act mainly on cellulose and hemicelluloses. After pyrolysis, the char weight increased with K up to 25.86 and 15.23 % for heating rates of 10 and 20 K min^{-1}, respectively. FTIR and XRD showed that potassium did not significantly impact the structure or the crystallinity of wood at ambient conditions. The obtained results provide a novel insight into the role of potassium in the thermal treatment of biomass, with a better understanding of the thermal degradation mechanisms. This information could help to reduce the operating time and/or temperature, thus rendering torrefaction a green method for waste wood valorization.

1. Introduction

The exponential increase of the world's population and the expansion of industries lead to increased energy demand. Subsequently, renewable energy sources such as solar, wind, hydropower, and bioenergy have been considered potential

* Corresponding authors at: Université de Lorraine, INRAE, LERMaB, F-88000 Epinal, France
** Corresponding author at: Department of Aeronautics and Astronautics, National Cheng Kung University, Tainan, 701, Taiwan.
E-mail addresses: larissa.richa@univ-lorraine.fr (L. Richa), anelie.petrissans@univ-lorraine.fr (A. Pétrissans), weihsinchen@gmail.com, chenwh@mail.ncku.edu.tw (W.-H. Chen).

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Nomenclature

Abbreviations

VM	Volatile matter(wt% dry basis)
FC	Fixed carbon (wt% dry basis)
HHV	Higher heating value (MJ/kg)
TGA	Thermogravimetric analysis
DTG	Derivative thermogravimetric curve (wt%.s^{-1})
DTG_{max}	Maximum point of DTG (wt%.s^{-1})
DTG''	Second derivative of TG (wt%.s^{-2})
FTIR	Fourier-Transform infrared spectroscopy
XRD	X-ray diffraction analysis

Molecules

CO_2	Carbon dioxide
C	Carbon
O	Oxygen
H	Hydrogen
N	Nitrogen
Na	Sodium
K / K^+	Potassium / Potassium ion
Ca	Calcium
Mn	Manganese
Mg	Magnesium
KCl	Potassium chloride
K_2SO_4	Potassium sulfate
KOH	Potassium hydroxide
K_2CO_3	Potassium carbonate

Greek letter

β	Heating rate (K min^{-1})

Symbols

T_i	Initiation temperature (°C) at 5% weight loss
T_p	Peak temperature corresponding to DTG_{max} (°C)
W_R	Residual weight at 850°C (wt%)
$T_{onset\ hc}$	Onset temperature of hemicelluloses (°C)
$T_{shoulder}$	Maximum degradation temperature of hemicelluloses (°C)
$T_{offset\ c}$	Final degradation temperature of cellulose (°C)
Cr_I	Crystallinity index (%)
I_{002}	Maximum intensity peak at the crystalline plane between 21° and 23° (a.u.)
I_{am}	Minimum intensity at the amorphous plane between 17° and 20° (a.u.)

alternatives to conventional fossil fuels. The primary purpose of renewable energy is to limit the negative environmental impact of burning fossil fuels (Manzano-Agugliaro et al., 2013). Choosing wood energy over fossil fuel can effectively cut CO_2 emissions and is a potential solution for global warming mitigation (Sulaiman et al., 2020). It is mainly valorized in combustion in suspension-fired boilers (Yin, 2020). However, boilers face technical issues when operating with biomass, among which is biomass's difficult and energy-consuming grinding (Bashir et al., 2012). Furthermore, using biomass in boilers results in high particle matter emissions and other technical issues such as biomass transportation cost, particle size heterogeneity, and differences in properties compared to coal (Gil and Rubiera, 2019; Sippula et al., 2017). Therefore, despite its many advantages, bioenergy still requires extensive and unbiased optimizations to overcome its limitations (Aghbashlo et al., 2022).

Torrefaction is a thermochemical conversion process where biomass is heated in an inert atmosphere at 200–300 °C. It effectively upgrades biomass and improves solid biofuel quality, also known as biochar (Chen et al., 2021a, 2015). It is recommended as an effective pretreatment for biomass use in the energy sector (Brachi et al., 2021). Torrefaction can effectively reduce the moisture content and the atomic ratios of O/C and H/C. Furthermore, it lifts wood's calorific properties and improves grindability (Chen et al., 2021b; Yek et al., 2021). Torrefied wood can also be used for construction without the detrimental effects of using toxic chemicals to make it withstand environmental conditions (Haloni and Vergnaud, 1997). Consequently, torrefied wood can be used for construction first, and then instead of being discarded at the end-of-life, it could be used for heat/power generation. Energy conversion processes generate waste heat between 200–300 °C, which can be recovered and used for torrefaction, thus achieving a sustainable cycle (Chen et al., 2022a).

Biomass thermal decomposition characteristics change during torrefaction and pyrolysis (Li et al., 2023). The variance depends on its three main components: hemicelluloses, cellulose and lignin (Ong et al., 2021). Hemicelluloses are a group of saccharides, including xylose, glucose, galactose, etc. They are amorphous and contain branches that allow them to be degraded at a low-temperature range of 220–315 °C. Cellulose is a long glucose polymer, ordered and semi-crystalline, containing crystalline and amorphous forms. It has more substantial thermal stability and is degraded in a temperature range of 315–400 °C. At the same time, lignin has a complex structure, full of aromatic bonds with branches. Therefore, it has a broad degradation range of 100–900 °C (Yang et al., 2007; Yu et al., 2017). The polymers are linked through hydrogen bonds, covalent linkages, etc. (Jin et al., 2006).

Wood's composition also includes minerals that influence the thermal degradation mechanisms (Dai et al., 2019). Five of them were proven to have the highest impact on biomass pyrolysis: Na, K, Ca, Mn, and Mg (Aho et al., 2013). Studies on organically bonded minerals determined that K and Na had the most dominant effect on torrefaction by increasing the weight loss between 240 °C and 280 °C (Khazraie Shoulaifar et al., 2016; Mahadevan et al., 2016). Additionally, even tiny quantities of these two minerals (0.1 wt%) will suppress levoglucosan formation. In contrast, Mg, Ca, and Mn had less influence (Khazraie Shoulaifar et al., 2016; Mahadevan et al., 2016). Potassium is a mineral with a nutritive role essential for plant growth (Fromm, 2010) and is in the form of an ion (K^+) in the greenwood, which could be mobile or attached to some functional groups, or as dissolved salts (Yu and Zhang, 2001). Once dried, potassium ion in wood makes linkages that form salts such as K_2CO_3, KOH, KCl, and K_2SO_4 (van Lith et al., 2008). Zhang et al. (2019) compared the effects of potassium and magnesium on the products at torrefaction temperatures below 270 °C. They reported that potassium increased the carbon content in solids due to deoxygenation. Both K and Mg promoted the formation of small-molecule gases by catalyzing the decomposition of larger liquid molecules, with K being the dominant catalyst.

In pyrolysis, potassium inhibits the formation of levoglucosan, and therefore, the interaction of potassium and cellulose leads to more stable products instead of tar formation (Nishimura et al., 2009; Wang et al., 2010). On an industrial scale, tar is an undesired byproduct of torrefaction, and its removal is necessary to avoid clogging pipes and decreasing the unit's failure rates (Chen et al., 2021c; Rabou et al., 2009). The potassium remaining in the char catalyzes combustion, achieving a higher carbon burn-out conversion (Jones et al., 2007). The potassium that remains in the char acts as a base catalyst and promotes ring-opening (Ryu et al., 2020). In addition, the produced biochar is highly porous and is efficient for soil amendment (Ajeng et al., 2020; Ray et al., 2021) and mercury capture in flue gas (Čespiva et al., 2023). When enriched with potassium, biochar can be valorized as a natural fertilizer essential for plant growth (Fachini et al., 2022; Seo et al., 2022). On an industrial scale, tar removal is necessary to avoid clogging pipes and decreasing the unit's failure rates (Rabou et al., 2009). Furthermore, Di Blasi et al. (2017, 2018) reported that potassium improves the exothermic reactions during pyrolysis in a packed bed and leads to a beginning of a self-sustainable process.

Potassium is a key factor in combustion since it increases decomposition kinetics and changes the products' composition, implying an alteration in the reaction mechanism. It causes heterolytic ring fission and cracks reactions that favor char production and low molecular weight products over furans and levoglucosan (Nowakowski et al., 2007; Patwardhan et al., 2010). The potassium remaining in the char catalyzes combustion, achieving a higher carbon burn-out conversion (Jones et al., 2007). Subsequently, the produced biochar is enriched in minerals and carbon that can be valorized for soil amendment (Chia et al., 2014). However, the volatilization of potassium risks increasing the slagging behavior and corrosion of the equipment (Nutalapati et al., 2007; Wang et al., 2017). Therefore, depending on the desired application, lower heating rates and operating at temperatures between 750–850 °C are recommended to avoid volatilization of K (Hu et al., 2019; Lee et al., 2022). These temperatures are considered optimal to safely benefit from the improvements provided by K-catalyzed thermochemical conversion processes (Wu et al., 2011).

Different torrefaction performances vary with the composition and K^+ content variability between wood species. The literature found a duality in the role of potassium where at low temperatures (torrefaction), it catalyzes the wood's degradation (Yang et al., 2006; Zhao et al., 2020), and at higher temperatures (pyrolysis), it favors char formation (Wang et al., 2022; Wongmat and Wagner, 2022). The area between the two effects remains ambiguous and needs exploring. Due to the stated inconsistent factors, it is desired to predict the torrefaction behavior and understand the factors that lead to the varying behavior of potassium. Therefore, this study aims to better understand the influence of potassium on wood torrefaction and lignocellulosic components. It explores the effects of torrefaction duration, temperature, and chemical composition on thermodegradation kinetics. The objective is to help optimize torrefaction as a pretreatment for power or heat generation by providing a deeper understanding of the reaction mechanisms.

2. Materials and methods

2.1. Sample preparation

The selected wood species for this study was Beech wood (*Fagus sylvatica*) since it is abundant but has limited applications in the French market. It was obtained from Vosges region in France (*Vosges PromoBois sawmill*). The cellulose source used was *Whatman Ashless* filter paper, d = 42.5 mm. It consisted of high purity α-cellulose (>99%) and was used in the literature to represent wood's cellulose (Khazraie Shoulaifar et al., 2016; Nishimura et al., 2009). Beech xylan (*Sigma Aldrich*) was selected for the hemicelluloses existing in beech (Macedo et al., 2018; Shen et al., 2020), and lignin was obtained from *Domtar Corporation, USA*.

According to a procedure commonly adopted in the literature, potassium was inserted into the biomass through chemical impregnation using K_2CO_3 (Khazraie Shoulaifar et al., 2016; Nishimura et al., 2009). The potassium carbonate K_2CO_3 employed was obtained from *Sigma Aldrich* with 99.99% purity. Based on the literature, carbonate had the slightest effect on torrefaction among various salts used for impregnation, while the cation in alkali metals is believed to be the main catalyst of biomass (Patwardhan et al., 2010; Yang et al., 2006). As a consequence, the dominant impact observed in the experiments corresponds to K^+.

The impregnation solutions were prepared by dissolving K_2CO_3 with deionized water according to the desired concentrations (0.004, 0.008, and 0.012 M). The samples were labeled according to the K_2CO_3 concentration. Dry powdered beech wood, cellulose, xylan, and lignin samples were potassium-impregnated. The beech wood blocks were ground to powder using a knife-mill SM100 (*Retsch, Germany*) equipped with trapezoidal meshes of 0.5 mm. The samples were impregnated by mixing 2 g of oven-dried samples with K_2CO_3 solution using a mixing ratio of 10 mL g^{-1}. The mixture was stirred for 1 h at ambient conditions before being filtered using Büchner vacuum filtration. The sample was then placed in the oven at 60 °C until weight stabilization. Since xylan was difficult to filter, it was immediately dried in the oven following the impregnation.

2.2. Physicochemical characterization

The proximate analysis of raw beech was obtained on an anhydrous basis in accordance with ISO-18122 (NF EN ISO 18122, 2015a), ISO-18123 (NF EN ISO 18123, 2015b), and ISO-18124 (NF EN ISO 18134, 2022) respectively, for the ash, the volatile matter (VM), and moisture content (MC). The fixed carbon (FC) was calculated by difference (FC = 100 - ash - VM - MC). Each measurement was performed in triplicate, and the average value was computed along with its standard deviation: $\sqrt{\frac{\sum(X-X_{av})^2}{n}}$; where X is the value measured (wt%), X_{av} is the average value (wt%), and n is the number of trials. The elemental composition of the raw beech was determined using a *PerkinElmer 2400 Series II CHNS/O* elemental analyzer performed on a dry-ash-free basis. The percentages of hydrogen (H), carbon (C), and nitrogen (N) were experimentally obtained and represented as an averaged value of the triplicate with a standard deviation. The oxygen (O) content was obtained by difference ($O = 100 - (C + H + N)$).

The chemical composition of beech was obtained using NREL/TP-510-42619 (NREL/TP-510-42619, 2005) for the extractives and the Klason method NREL/TP-510-42618 (NREL/TP-510-42618, 2012) for the lignin. After complete delignification, the wood is heated, and holocelluloses are extracted using sodium chlorite and acetic acid solutions, followed by an alkaline attack with sodium hydroxide to acquire the α-cellulose eventually. The higher heating value (HHV) for solid fuel was determined using ISO-18125 (NF EN ISO 18125, 2017). In brief, it consists of packing 0.5 g of the sample into a pellet placed in the bomb calorimeter (*Parr 6100 Calorimeter*) filled with pure oxygen. The sample is combusted in the bomb, and the equipment computes the HHV directly. The potassium content in the raw and K-impregnated beech samples was determined by inductively coupled plasma optical emission spectroscopy (*ICP-AES 720/725 Agilent*) using 200 mg of sample (± 0.5 mg) that was mineralized before the measurement.

2.3. Thermogravimetric analysis

2.3.1. Torrefaction

A thermogravimetric analyzer was used to analyze the wood's thermodegradation according to a specific temperature profile. A high-precision thermobalance tracks the sample's mass evolution according to the treatment duration and temperature. The *Mettler Toledo TGA-2* was operated with an inert gas (N_2) flow of 100 mL min^{-1}. The ground samples were oven-dried for 24 h at 105 °C. Then 5 mg of the sample was loaded in an alumina crucible in the thermogravimetric analysis (TGA) machine. The system was heated with a heating rate of $\beta = 20$ K min^{-1} from 50 to 105 °C. Then it was held at this temperature for 30 min to remove moisture, followed by heating the sample to each of the desired torrefaction/pyrolysis temperatures (250, 300, and 380 °C) with the same heating rate. After reaching the desired temperature, it was held for 2 h. The purpose of the isothermal step was to observe the change in the degradation kinetics with potassium. Finally, the sample was pyrolyzed to 850 °C using the same heating rate of 20 K min^{-1}. The time derivative of the TGA curve was calculated and plotted as the differential thermogravimetric (DTG) curve. The TGA curves were duplicated, and a low relative error (<2 wt%) was obtained, showing repeatable results.

2.3.2. Pyrolysis

Pyrolysis experiments were also performed, heating the sample with a constant heating rate. The purpose of this experiment was to observe in detail the decomposition of lignocellulosic components with increased potassium concentration. The pyrolysis experiments were conducted similarly to the torrefaction until the moisture removal step. Then the temperature was increased from 105 to 850 °C with a heating rate of $\beta = 10$ K min^{-1} (El-Sayed and Khairy, 2015; Pan et al., 2015) or $\beta = 20$ K min^{-1} (Bach and Chen, 2017; Lu et al., 2013). The higher heating rate is used to obtain a sharper peak intensity, and the lower one is chosen to observe better the separation of the curves (larger peaks). The experiments were performed on beech wood (raw and potassium impregnated). In addition to TGA and DTG curves, the second derivative (DTG'') was also calculated to determine each biopolymer's more precise decomposition range. Through the DTG'' the exact temperature corresponding to the hemicelluloses shoulder could be determined, as well as the temperature of the end of the celluloses degradation/ main lignin decomposition. The experiments were triplicated with a relative error below 2%, and the average curves were elaborated.

2.4. Chemical analysis

2.4.1. Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) was utilized to qualitatively investigate the effect of potassium impregnation on the chemical structure of beech and its constituents. Using a Nicolet iS10 spectrometer equipped with an attenuated total reflectance (ATR) device, the FTIR spectra were obtained for the raw and impregnated samples of beech, cellulose, xylan, and lignin. All spectra were normalized according to the CH stretch at 2900 cm^{-1} (Gonultas and Candan, 2018). The obtained spectra are an average of 32 scans per sample.

2.4.2. X-ray diffraction

An Empyrean Malvern PANalytical Powder X-ray Diffractometer was used to obtain the diffraction patterns of raw and impregnated wood samples. Powder X-ray diffraction was measured between 5° and 60°. The patterns reported correspond to the average of 10 diffractograms per sample. Each measurement was performed in triplicate, and the average value was recorded with its standard deviation.

Different methods exist to determine the crystallinity index, all of which pivot around the same principle of finding the amorphous-to-crystalline ratio (Šoštarić et al., 2020; Wang et al., 2013). In this article, the crystallinity index was calculated according to the Segal Empirical Method (Eq. (1)) since it takes into account each curve's intensity peaks (Chen et al., 2022b):

$$Cr_I = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \tag{1}$$

where Cr_I is the crystallinity index in %, I_{002} is the maximum intensity peak at the crystalline plane between 21° and 23°, I_{am} is the minimum intensity at the amorphous plane between 17° and 20°.

3. Results and discussion

3.1. Physicochemical properties

The properties of raw beech wood are shown in Table 1. The chemical composition obtained for the beech is comparable to the literature, where cellulose is the most abundant component (Bodîrlău et al., 2008; Candelier et al., 2013). To check the efficiency of the impregnation process, the K content in the different samples measured by the ICP-AES is also presented in Table 1. The results show a consistent increase of the potassium content in wood with the increased K_2CO_3 concentration in the impregnating solution. Potassium was increased more than 3 times its original content, ranging from 0.101 wt% in the raw beech sample to 0.310 wt% in the 0.012 M sample. The impregnation efficiency was different for each lignocellulosic component. It can be seen that xylan has the most K because it was not filtered after impregnation. The differences in K content after impregnating each lignocellulosic component can be attributed to the differences in molecule structure and powder texture.

3.2. Torrefaction

The thermogravimetric analysis of beech (TGA and DTG) during torrefaction is presented in Fig. 1. For the torrefaction at 300 °C, potassium had a significant role in the thermodegradation of the biomass (Fig. 1 b). By increasing the potassium content from the raw beech to 0.012 M, the weight decreased by 8.47% at the same time (82 min). The curves met at the same point around the end of the isothermal plate, corresponding to a solid yield of 32–34 wt%. After the intersection, the potassium that previously catalyzed the wood degradation increased char formation. The double roles of potassium were reported by Yang et al. (2006), stating that at temperatures lower than 315 °C, potassium addition increased weight loss, while above 315 °C, it produced more char. Nevertheless, the results found in this study demonstrated that the treatment duration was also responsible for the observed effects of potassium. The reaction time and temperature were reported to influence torrefaction strongly (Trubetskaya et al., 2017). Therefore, it was reasonable that the impact of potassium on the torrefaction also depended on these two variables.

At 250 °C torrefaction (Fig. 1a), the K-impregnated samples did not differ significantly from the raw biomass. Yet it still catalyzed the degradation reactions of the wood to some extent during the isothermal step. Then, during the pyrolysis step, the curves intersected and inverted at 380 °C. This result clearly shows the two distinct roles of potassium in the different stages of thermal degradation. Moreover, potassium addition promoted char formation in the samples treated

Table 1
Beech wood and lignocellulosic components properties.

Material	Beech wood
Proximate analysis (wt% anhydrous basis)	
Ash	0.59 (0.06)[a]
Volatile matter (VM)	77.49 (0.02)
Moisture content (MC)	3.71 (0.12)
Fixed carbon (FC) (by difference)	18.21
Elemental analysis (wt% dry-ash-free basis)	
C	55.66 (1.83)
H	6.10 (0.10)
N	0.55 (0.06)
O (by difference)	37.69
Chemical composition (wt%)	
Cellulose	47.27 (0.85)
Hemicelluloses	23.04 (0.74)
Lignin	23.7 (0.25)
Extractives	2.67 (0.27)
HHV (MJ.kg^{-1})	18.5 (0.2)
K (wt%) anhydrous basis	
Beech wood	
Raw	0.101
0.004 M	0.176
0.008 M	0.230
0.012 M	0.310
Cellulose	
Raw	0.001
0.004 M	0.155
0.008 M	0.162
0.012 M	0.248
Xylan	
Raw	0.020
0.004 M	0.369
0.008 M	0.631
0.012 M	0.965
Lignin	
Raw	0.101
0.004 M	0.237
0.008 M	0.421
0.012 M	0.561

[a]Standard deviation.

at 380 °C for 2 h (Fig. 1c). After reaching the isothermal step at 380 °C (approximately 49 min), the char yield increased by 3.3 wt% from the raw to 0.012 M sample, stemming from polycondensation (Safar et al., 2019). The conversion of monomers and oligomers catalyzed by potassium increases the production of char and volatiles (Szabó et al., 1996).

In addition, for all the torrefaction temperatures, the curves intersected at the same point (32–34 wt% remaining). Under these conditions, most hemicelluloses and cellulose are degraded, leaving a relatively higher lignin content (Safar et al., 2019). The effect of potassium may depend on the wood's chemical composition. After a specific lignin content, potassium either inhibits thermal degradation or alters the reaction mechanism. It is speculated that in a sample where lignin becomes the dominant component, lignin-K interactions promote deoxygenation reactions, favoring the formation of highly aromatic products (char). This result conforms with the study of Saleh et al. (2013), stating that torrefaction of samples rich in lignin produced more char when adding potassium. This impact could be attributed to multiple phenomena: (1) For wood particles larger than 0.2 mm, the tars that are produced during the heating lead to secondary reactions that result in char formation (Trubetskaya et al., 2017), (2) potassium could impact the interactions between lignin and the other biopolymers or their byproducts leading to subsequent reactions that promote char formation (Wang et al., 2022), (3) K_2CO_3 in lignin, leads to the cleavage of β-O-4 bonds into G-type aromatic compounds resulting in depolymerization into small molecular weight phenols that undergo oligomerization that results in char formation (Toledano et al., 2014; Zhang et al., 2020).

The TGA of the separate wood components (Fig. 2) displayed that the presence of potassium changed the degradation behavior of cellulose and hemicelluloses. The temperature of maximum degradation (attributed to cellulose decomposition) corresponding to the DTG peak (Fig. 2 b) shifted from 300 °C to around 280 °C, comparable to that of hemicelluloses (Fig. 2a). This phenomenon is consistent with the literature (Szabó et al., 1996; Yang et al., 2006) that found an overlap between cellulose and hemicellulose peaks with the addition of K_2CO_3. Close similarities in the obtained TGA and DTG profiles of cellulose were reported in the literature (Macedo et al., 2018). Therefore, reducing the temperature of the maximum degradation of wood (Fig. 1) could be partially attributed to the effect of potassium on cellulose that shifts the DTG peak to a lower temperature/time.

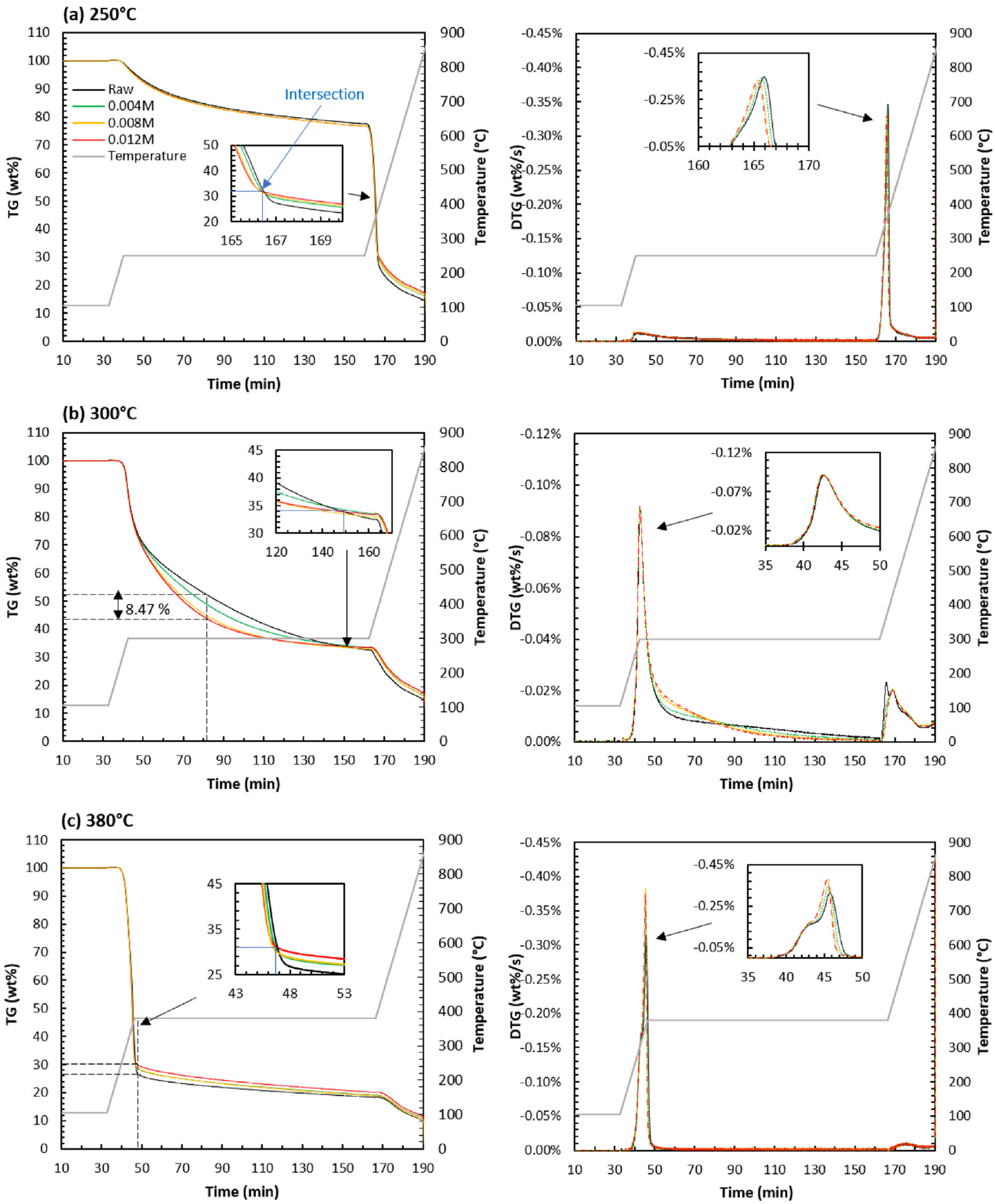

Fig. 1. TGA and DTG of beech samples with different potassium contents during torrefaction at 250 °C (a), 300 °C (b), and 380 °C (c).

The torrefaction at 300 °C of potassium-impregnated xylan (Fig. 2c–d) increased the char yield which coheres with the results of Khazraie Shoulaifar et al. (2016) using galactoglucomannan as hemicelluloses. However, Macedo et al. (2018) stated that potassium had a negligible effect on xylan. As for lignin, the TGA (Fig. 2e) and DTG (Fig. 2f) showed unimportant variations with impregnation. Shen et al. (2020) noted that the catalyzing effect of potassium compounds on lignin decomposition was insignificant. The insignificant variations could result from isolating the lignin as a separate component. The lignocellulosic components interact mostly with lignin (Yu et al., 2017). For instance, lignin interacts with

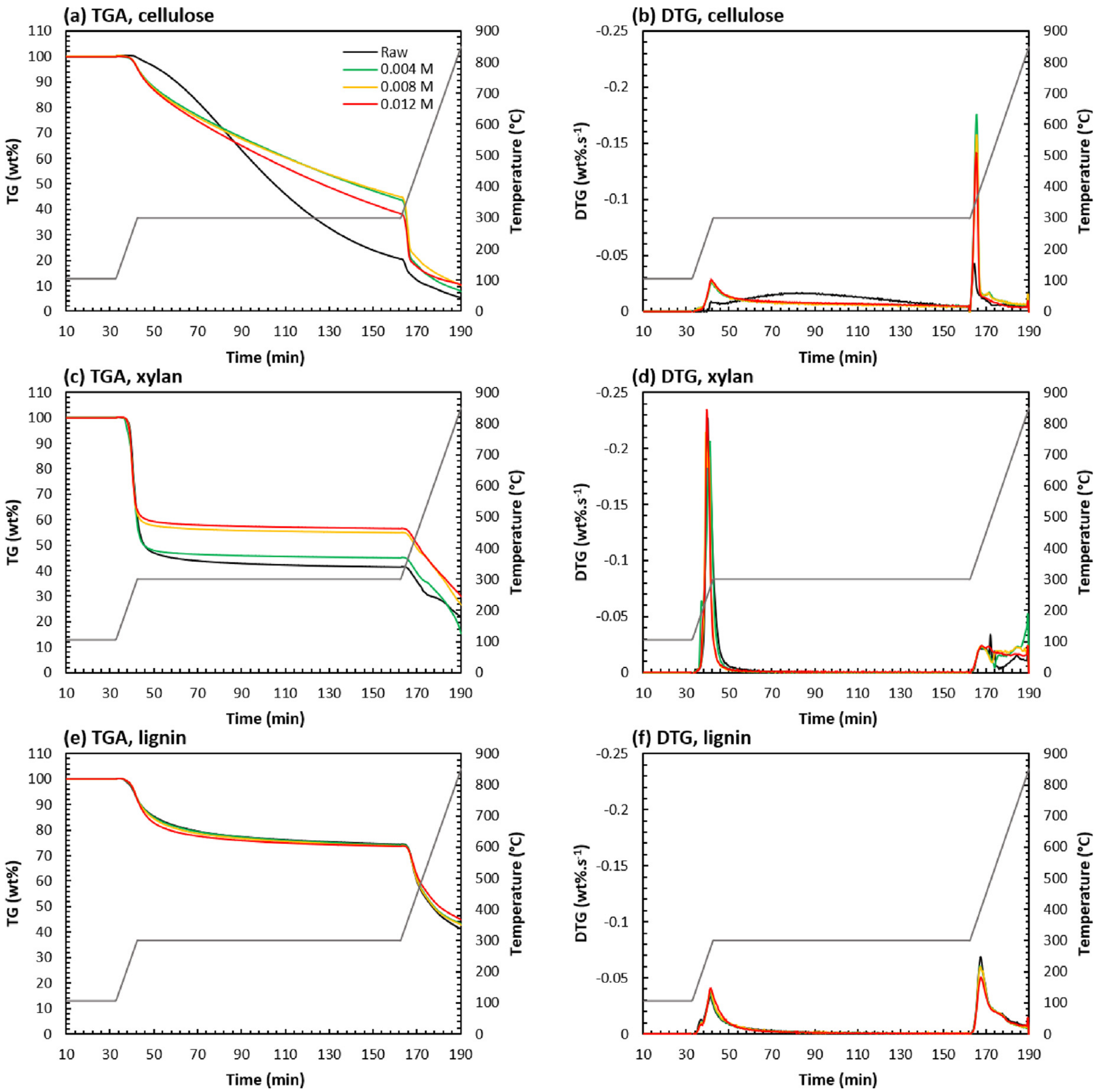

Fig. 2. TGA (a,c,e) and DTG (b,d,f) of lignocellulosic components torrefaction at 300 °C.

cellulose during thermal treatment, inhibiting levoglucosan's polymerization (Hosoya et al., 2007). Therefore, potassium could be acting on some of the lignin's interactions which go unnoticeable when analyzing lignin by itself. Moreover, Shen et al. (2020) reported that the degradation of xylan and cellulose is onset earlier for the K-rich samples. It correlates with the study of Lin et al. (2021) suggesting that potassium initiates the degradation of hemicelluloses at lower temperatures. Guo et al. (2016) developed a model for the degradation of wood during pyrolysis with potassium impregnation. The study reported that the potassium accelerated hemicellulose decomposition in the initial stage of pyrolysis and intensified cellulose degradation in the main stage.

3.3. Pyrolysis

The TGA results (Fig. 3a–b) confirm that the intersection occurs at one point (∼31wt%), regardless of the heating rate and the intersection temperature: 370 °C for 10 K min^{-1} and 380 °C for 20 K min^{-1}. This point reinforces the supposition that the chemical composition of wood contributes to the change of potassium's role from catalyzing weight loss to facilitating char formation. Like torrefaction, adding potassium to the samples shifted the DTG peaks (Fig. 3c-d) towards lower temperatures and reduced the hemicellulose shoulder. The DTG'' (Fig. 3e–f) followed the same profile as DTG,

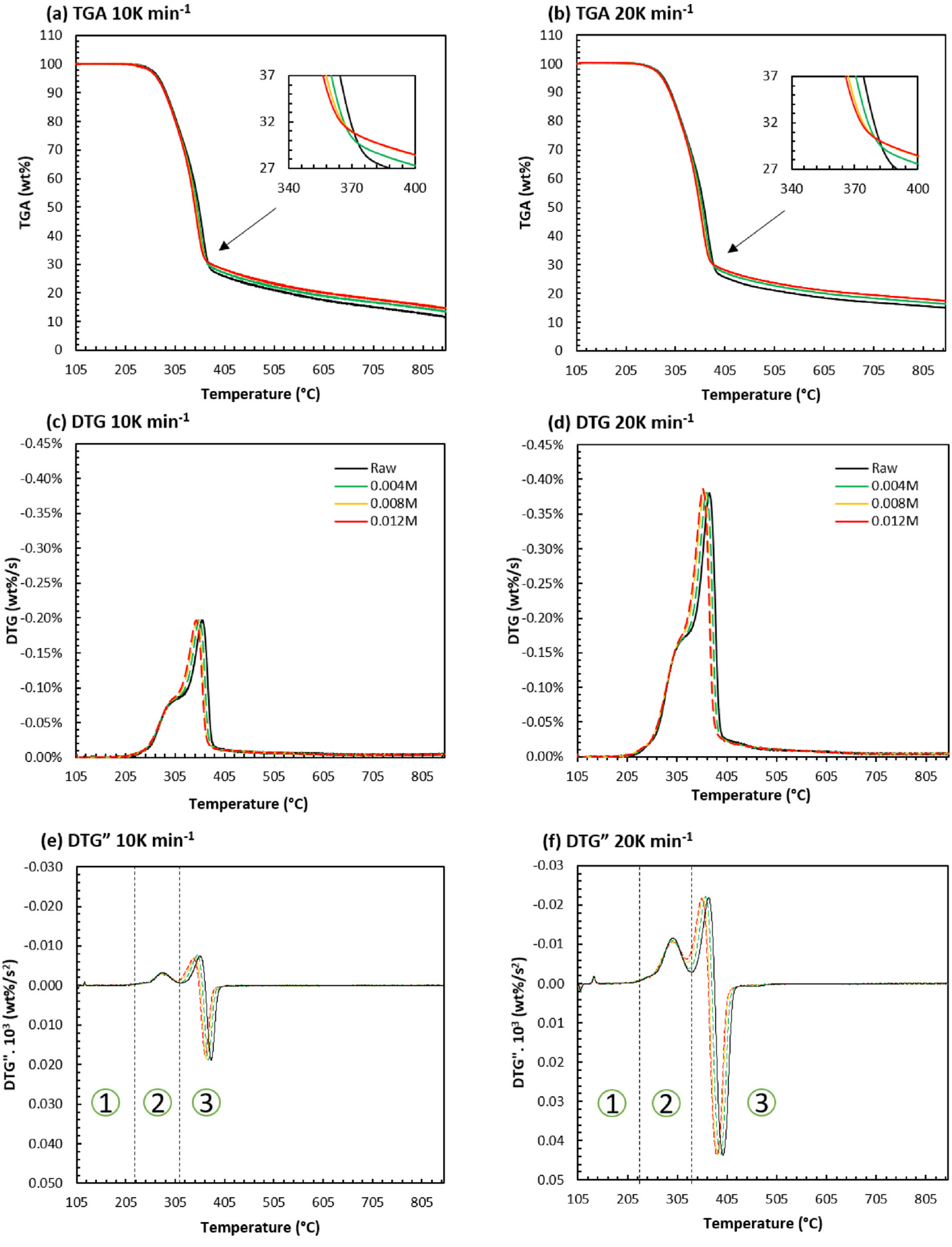

Fig. 3. Thermogravimetric results of beech pyrolysis (a) TGA 10 K min^{-1} (b) TGA 20 K min^{-1} (c) DTG 10 K min^{-1} (d) DTG 20 K min^{-1} (e) DTG" 10 K min^{-1} (f) DTG" 20 K min^{-1}. Section 1 is the moisture removal zone, 2 is the main zone of hemicelluloses decomposition, and Section 3 consists of cellulose decomposition (peak) and lignin degradation (trough).

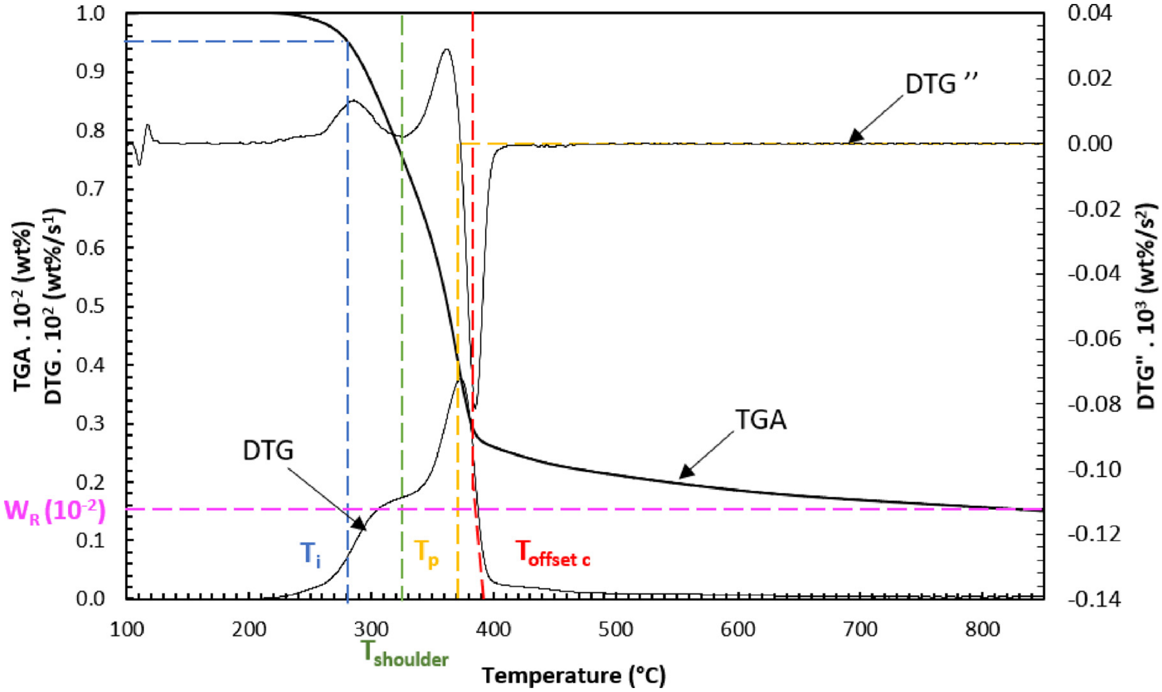

Fig. 4. Thermogravimetric parameters determination. The principal y-axis corresponds to TG (10^{-2} wt%) and DTG (10^{2} wt%.s^{-1}), the x-axis is the temperature, and the secondary y-axis is DTG" (10^{3} wt%.s^{-2}).

Table 2
Thermogravimetric parameters evolution with the increase of potassium concentration during pyrolysis at two heating rates.

β (K min^{-1})	Sample	T_i (°C)	T_p(°C)	W_R (wt%)	$T_{shoulder}$ (°C)	$T_{offsetc}$ (°C)
10	Raw	272.8	359.8	11.6	323.3	378.2
	0.004 M	270.1	354.0	13.6	308.8	372.7
	0.008 M	269.8	350.0	14.7	300.3	369.6
	0.012 M	269.3	348.3	14.6	301.0	367.4
20	Raw	281.3	370.3	15.1	322.0	389.8
	0.004 M	279.7	364.3	16.3	316.3	384.5
	0.008 M	278.0	359.3	17.5	313.7	379.7
	0.012 M	278.0	356.7	17.4	312.3	378.3

where the main cellulose decomposition zone (3) was primarily impacted by the increase of K content. The peaks moved to lower temperatures towards the range of hemicelluloses degradation (2) for both heating rates used. The effect was more prominent for the higher heating rate $\beta = 20$ K min^{-1}. The shift validates that the celluloses degrade at lower temperatures with potassium, as seen in torrefaction.

The pyrolysis parameters representing the evolution of the degradation of wood and lignocellulosic components were determined according to Fig. 4, and the values are presented in Table 2. The initial temperature (T_i) is measured after 5 wt% conversion, representing the initiation of pyrolysis linked to hemicelluloses degradation. The peak temperature (T_p) is the maximum degradation temperature at DTG$_{max}$ (inflection point in DTG"). The weight residue (W_R) is defined as the weight of the sample remaining at the end of the pyrolysis; in this case it is at 850 °C (Guo et al., 2016; Zhou et al., 2013). From the DTG" the following parameters were deduced: $T_{shoulder}$ is the temperature of the maximum hemicelluloses degradation determined by the local minimum between the two peaks. $T_{offset\ c}$ corresponds to the temperature dominated by the final phase of cellulose decomposition obtained by extrapolating the minimum of DTG" and forming a slope with 0 of the DTG axis (Grønli et al., 2002).

As expected, potassium catalyzed the wood degradation in the first stage, where T_i decreased by 3 °C with an almost equal temperature between 0.008 and 0.012 M. This indicates that a certain concentration of potassium (0.008 M) was required to weaken hydrogen bonds, after which the glycosidic linkage can be broken (Chen et al., 2022c). Beyond 0.008 M (0.230 wt% K), potassium's impact on T_i remains constant, which suggests a saturating effect of the catalytic action of K on T_i. With the DTG", a differentiation between the overlapping peaks of hemicelluloses and celluloses decomposition was possible. The main degradation of hemicelluloses occurred between 300 and 323 °C, while that of celluloses was between 378 and 390 °C. The tangible effect of potassium on triggering hemicellulose degradation was shown in $T_{shoulder}$ where it

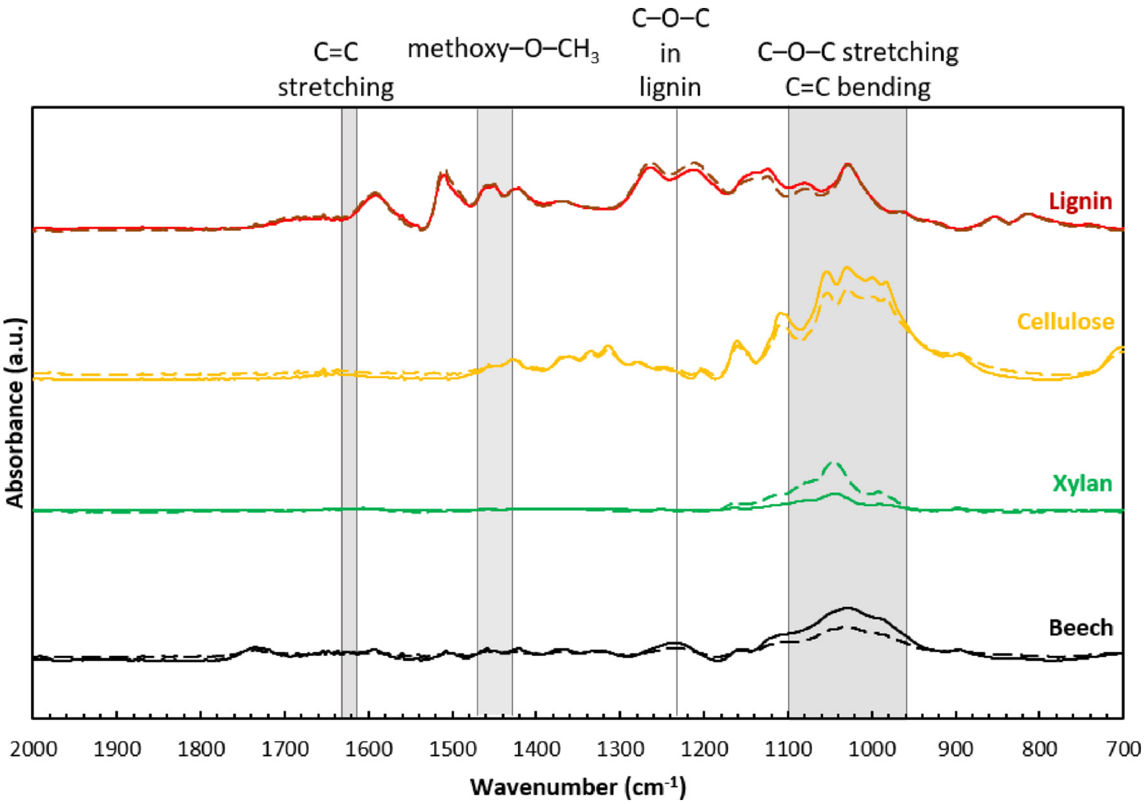

Fig. 5. FTIR spectra of beech, xylan, cellulose, and lignin. The continuous line is the raw sample, and the dashed one is the 0.004 M sample.

was remarkably reduced, especially at the lower heating rate (Lin et al., 2021), thus highlighting the efficiency of high K content to operate at lower temperatures during torrefaction/pyrolysis. For both heating rates, increasing potassium from raw to 0.012 M decreased T_p (mainly attributed to the degradation of cellulose) by 11 and 14 °C, respectively, for $\beta = 10$ K min^{-1} and 20 K min^{-1}.

Opposingly, W_R increased with potassium, which agrees with the literature (Persson and Yang, 2019). With the addition of K from the raw to 0.012 M, W_R increased more for the lower heating rate (25.86% increase) than the higher one (15.23% increase). This correlates with the study of Trubetskaya et al. (2017), which reported that potassium alters the activation energy for char production, especially at a lower heating rate. Zhou et al. (2017) found that adding potassium salts decreased T_p and increased W_R. This behavior was attributed to potassium facilitating the ring-opening reactions and glycosidic link breaking. Potassium possibly increased the char yield by modifying pyrolytic reaction pathways. It could promote polymerization reactions involving alkene intermediates via the ionic mechanistic route (Evans and Milne, 1987). Saddawi et al. (2012) reported a linear fit trend for char increase with the addition of potassium acetate. However, the regression coefficient was 0.55. Moreover, they stated that the apparent reaction rate of willow pyrolysis reached a saturation point at 4 wt% (K) due to the fulfillment of all active sites. In this study, at 0.012 M, W_R became almost equal to that of 0.008 M, which complies with the saturating effect stated in the literature. However, the linear regression of W_R as a function of K content had a higher R^2 coefficient of 0.80 and 0.83, respectively, for $\beta = 10$ K min^{-1} and $\beta =$ 20 K min^{-1}. It can be assumed that the potassium bonds to carboxylic groups during torrefaction and facilitates their degradation (Khazraie Shoulaifar et al., 2012). However, after a certain concentration in wood, K bonds to phenolic and carboxylic groups in lignin, that are harder to degrade during torrefaction (Khazraie Shoulaifar et al., 2016).

Since cellulose is degraded at higher temperatures, the two heating rates had the same effect on its degradation. Hence, $T_{offset\ c}$ was reduced by 11 °C from raw to 0.012 M according to the torrefaction experiments and the literature (Silveira et al., 2022; Wang et al., 2010).

3.4. Fourier transform infrared spectroscopy

In the FTIR spectra displayed in Fig. 5, potassium led to minor modifications of the wood's chemical structure and some of its biopolymers at ambient conditions. Therefore, the impact of potassium occurs with increasing temperature during torrefaction and pyrolysis (Sections 3.2 and 3.3). As observed in Fig. 5, lignin displays signals corresponding to

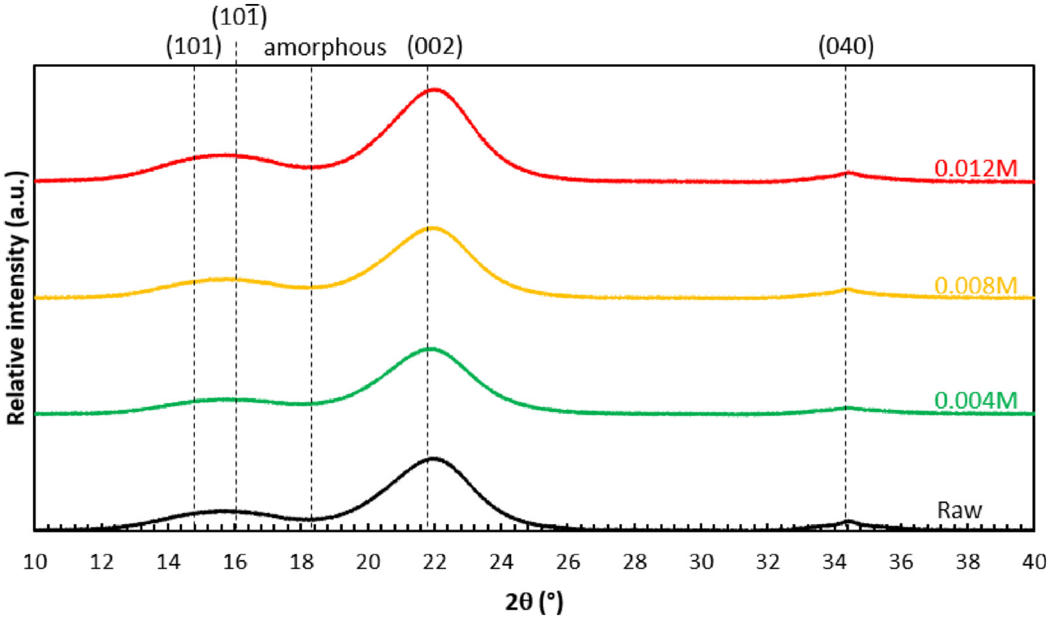

Fig. 6. XRD spectra and crystallographic planes of beech.

C-O-C (1232 cm^{-1}), methoxy-O-CH$_3$ (1470–1430 cm^{-1}), and aromatic C=C stretch (1632–1613 cm^{-1}) characteristic of its complex structure (Yang et al., 2007). According to the FTIR results, potassium impregnation had little to no impact on the lignin structure.

The K increased slightly influences cellulose, xylan, and beech in 1150–920 cm^{-1}. The band at 1100 cm^{-1} is attributed to the glycosidic symmetric vibrations of C-O-C in cellulose and hemicelluloses (Moosavinejad et al., 2019; Yang et al., 2020). The results indicated a minor degradation of cellulose due to the impregnation, possibly associated with the removal of amorphous domains. Potassium can interact with the glycosidic bonds of cellulose at ambient conditions and facilitates their cleavage during torrefaction, as stated in Section 3.2. The decreased peak intensity with potassium in the range 1200–900 cm^{-1} indicates a possible limitation of the production of large molecular volatiles with the addition of K_2CO_3 (Liu et al., 2008). The peak intensity decreased in beech since its main component was cellulose (Table 1). However, the band at 1120 cm^{-1} increased with potassium for xylan, possibly because the impregnation dissolved some amorphous branches in the sample. Moreover, the drying could have led to partial C-O-C degradation and condensation.

3.5. X-ray diffraction

Native cellulose in wood has four dominant crystalline planes (101, 10$\overline{1}$, 002, and 040) observable in XRD patterns. Wood cellulose also has an amorphous part corresponding to the local minimum between two peaks (Park et al., 2010; Popescu et al., 2011). The four crystalline planes correlating with literature were identified (Fig. 6) with two peaks overlapping between 15.44° and 15.91°, attributed to (101) and (10$\overline{1}$), 21.9° and 21.98° (002), 34.34° and 34.52° (040). The amorphous plane was distinguished at $2\theta = 17.99°–18.32°$.

The crystallinity index of beech varies between 86.8% (3.3%) for the raw sample and 85.5% (1.9%) for the 0.012 M sample. The change in crystallinity of wood with the addition of K_2CO_3 is below 2% and therefore is not considered significant. Therefore, the cellulose structure is not severely altered under the applied experimental conditions and using K_2CO_3 for impregnation. The impregnation with potassium does not impact the thermal degradation profile at torrefaction temperatures lower than 450 °C (Wang et al., 2013). Some sources in the literature reported a rise in biomass crystallinity after alkaline treatment, where the crystalline structure of the treated sample became more ordered than the control. However, the overall thermal stability of the biomass decreased with the alkali impregnation (Šoštarić et al., 2020; Xu et al., 2020).

4. Conclusions and prospects

The torrefaction experiments showed that potassium had two effects on wood's thermal degradation. Potassium had a significant impact on the torrefaction at 300 °C, in which it catalyzed the degradation of the sample. Though after 34% mass remaining, potassium promoted char production, possibly by breaking the glycosidic bonds and cleaving hydrogen bonds. It reduced the temperature of maximum degradation of cellulose due to the action of K^+ in weakening the hydrogen bonds. It also acted on the thermal decomposition of hemicelluloses by increasing char production. However, lignin was difficult to degrade, and the addition of potassium had little effect.

Pyrolysis experiments were conducted to observe detailed changes in the main degradation parameters. The addition of potassium triggered the thermal degradation of biomass at lower temperatures. Potassium acted by effectively reducing the peak temperature of beech, in which the degradation was at its highest level due to the promoted decomposition of cellulose and hemicelluloses. A saturating potassium concentration in biomass seemed to exist, after which the effect of potassium on the initiation temperature and the char yield was limited. This concentration was optimal for an efficient catalyzing role of potassium. From FTIR and XRD, potassium did not alter wood's crystallinity or structure, including its constituents at ambient conditions.

Based on the results obtained, the catalytic effect of potassium depends on the torrefaction temperature, duration, and chemical composition. Until now, the temperature was believed to be the only parameter that causes the duality in potassium's effect. This study demonstrates that after reaching a specific composition, potassium starts to improve char production, thus switching from the effect observed during torrefaction to the effect observed during pyrolysis, even when keeping the temperature constant.

By apprehending 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. Based on the intended use of wood, the species should be selected according to potassium content and chemical composition. High potassium content with lower lignin content reduces operating time and temperature during torrefaction, thus reducing the cost. Furthermore, the produced char is high in potassium salts, which are nutrients for soil, and could be consequently used as fertilizers.

In industry, wood boards are used; therefore, potassium's effect on wood's torrefaction should be tested on a larger scale using wood boards instead of powder. When changing the scale, the impregnation might be less efficient, and the thermal degradation profile may differ. Moreover, the study only uses small quantities of wood and therefore does not take into account the exothermic reactions that could be more visible for large samples. Therefore, future studies should be performed using wood boards to understand better the efficiency of the K-impregnation and torrefaction in industrial conditions. Moreover, a techno-economic analysis should be done to evaluate the feasibility of the process with the time/temperature gain compared to the expenses related to the impregnation. Future works should also look into the possible changes in char properties after potassium impregnation.

CRediT authorship contribution statement

Larissa Richa: Formal analysis, Methodology, Validation, Writing – original draft. **Baptiste Colin:** Conceptualization, Project administration, Supervision, Writing – review & editing. **Anélie Pétrissans:** Conceptualization, Funding acquisition, Project administration, Supervision, Writing – review & editing. **Ciera Wallace:** Data acquisition, Methodology. **Allen Hulette:** Data acquisition, Methodology. **Rafael L. Quirino:** Validation, Writing – review & editing. **Wei-Hsin Chen:** Funding acquisition, Validation, Formal analysis, Investigation, Writing – review & editing. **Mathieu Pétrissans:** Funding acquisition, Project administration, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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