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Potassium Carbonate as a Catalyst for Wood Torrefaction#

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ABSTRACT

Potassium carbonate (K_2CO_3) is known to influence the kinetics of degradation of lignocellulosic biomass. Its effect has been studied in the literature on wood particles, but its catalytic effect on wood boards remains unexplored. In this work, beech wood blocks were impregnated with solutions having different concentrations ranging from 0 (demineralized water) to 0.012 M of K_2CO_3. After torrefaction at 300°C for 15 min, potassium impregnated samples were degraded up to 7.49 wt% (0.012 M) more than the raw one. The impregnation procedure and torrefaction changed the wood's color, the desired aspect for construction. The increased HHV with torrefaction (around 24 MJ.kg^{-1} for 0.012 M impregnated samples) is attractive for energy production from end-of-life wood products. The obtained results validate the possibility of using potassium carbonate as a catalyst for wood torrefaction to reduce the torrefaction duration/temperature. Moreover, the torrefied wood has upgraded properties that make it useful for bioenergy production.

Keywords: Potassium carbonate, Torrefaction, Wood, Energy, Carbon neutrality

NONMENCLATURE

Abbreviations	
DSC	Differential scanning calorimeter
HHV	Higher heating value (MJ.kg^{-1})
db	Dry basis
Symbols	
W	Width (cm)
L	Length (cm)
t	Thickness (cm)
m_{loss}	Percentage of mass loss (wt%)
m_0	Initial mass before torrefaction (g)
m_f	Final mass after torrefaction (g)

1. INTRODUCTION

Achieving carbon neutrality is challenging and requires a lot of optimization in the use of natural resources [1]. Wood is widely used in construction; however, when it is coated with chemicals to make it stable over time, the residues are toxic to the environment [2]. Torrefaction is suggested as a new method to treat wood to improve its energetic and physical properties [3]. This process upgrades wood used in construction and allows it to be later used for power/heat generation [4,5]. This technique consists of heating the biomass in an inert atmosphere (nitrogen, flue gas, vacuum, etc) at 200-300°C. During torrefaction, wood is transformed through thermochemical reactions that increase its homogeneity, its resistance to fungi, its heating value, and reduces its density [6]. It is encouraged in France that issued a regulation urging the use of bio-sourced materials, including wood to reduce the carbon impact of new buildings [7]. Moreover, torrefied wood's transportation and combustion emit significantly fewer greenhouse gases (GHG) than raw ones [8,9].

Potassium (K) is a mineral vital for plant growth and therefore naturally present in the wood [10]. It was the subject of many studies to understand its effect on wood pyrolysis and combustion. However, a deeper understanding of potassium's role in torrefaction is needed, and more precisely on a larger scale than wood powder. To our knowledge, no studies have investigated the effect of potassium impregnation on wood blocks.

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In a previous work presented to the ICAE2021 [11], potassium was demonstrated to catalyze the degradation of wood with a short torrefaction time at 300 °C. The aim of this work is to scale up from wood powder used in the previous work to larger blocks. The objective is to understand the impact of potassium on the thermal degradation of wood blocks and on the heating value. It aims to give a second life to wood used in construction and reduce the carbon impact by valorizing it as a biofuel.

2. MATERIALS AND METHODS

2.1 Sample preparation

Beech wood (*Fagus sylvatica*) was used in this study as it is easy to impregnate. Beech boards were cut to blocks of 6 cm x 14 cm x 2 cm (W x L x t) and were then oven dried at 105 °C until mass stabilization.

Potassium carbonate (K_2CO_3) solutions were prepared for the impregnations with concentrations of 0.004 M, 0.008 M and 0.012 M and the impregnated samples were labelled accordingly. Additional samples were impregnated using the same procedure with demineralized water only and were labelled 'washed'. The samples were placed in a sealed tank where they were submerged in the corresponding solution. The impregnation was achieved by a cycle of vacuum for 30 min followed by a pressure cycle at 2 bars for 30 min. The impregnated wood was then air dried for 72 h and then placed in the oven at 105°C until a constant mass was achieved.

2.2 Torrefaction

The dry impregnated wood was torrefied in a reactor under a constant nitrogen flow of 100 mL.min^{-1}. The reactor consists of a stainless-steel cylinder, sealed with an input of nitrogen and an output that is linked to a water trap to remove tars. The reactor is heated inside a chamber equipped with an electrical resistance and a fan to homogenize the heat transfer across the surface of the reactor. Each sample was placed in the sealed reactor and heated from room temperature to 300 °C with a heating rate of 2 °C.min^{-1} close to what is generally used in industry. The temperature was then held at 300 °C for 15 min.

The mass loss was calculated as:

$m_{loss} = \frac{m_0 - m_f}{m_0} \times 100$; where m_{loss} is the mass loss (wt%), m_0 is the initial dry mass of untreated wood (g db), and m_f is the final mass of wood after torrefaction (g db).

2.3 Colorimetry

The color evolution is an indicator of the wood's degradation extent. The color changes with the impregnation and torrefaction were recorded using a colorimeter (*Konica Minolta Chroma Meter CR-410*). The color was measured in four sections covering both sides of the block and the average parameters were calculated. The representation is based on CIELAB three-dimensional space adopted for wood color quantification. The measured variables are L* ranging from 0 for pure black to 100 for pure white, a* is on the green-red axis where +a* is for red and -a* is for green, and b* located on the blue-yellow axis where +b* is for yellow and -b* is for blue. The overall difference in color was calculated at each point as $\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$ and the average value was computed [6].

2.4 HHV

The higher heating value (HHV) represents the gross energy of a fuel in combustion [12]. It was measured using *Parr 6100 Calorimeter* run under pure oxygen for complete sample combustion according to ISO-18125 [13]. Beech sample (raw, washed, and K-impregnated) was ground and dried then pressed into 1 g capsules for the analysis. The capsule was attached to the ignition thread and placed inside the bomb vessel of the calorimeter. The sample was burned and the produced energy per unit of mass of the sample was determined by the calorimeter. The experiments were duplicated and the average values were calculated.

3. RESULTS AND DISCUSSION

3.1 Torrefaction

The temperature profile is shown in Fig. 1. The maximum temperature inside the oven reached 291 ± 1.45 °C for all experiments. The mass loss results are shown in Fig.2 for 15 min of torrefaction at 300 °C. The raw and washed samples had almost equal mass losses

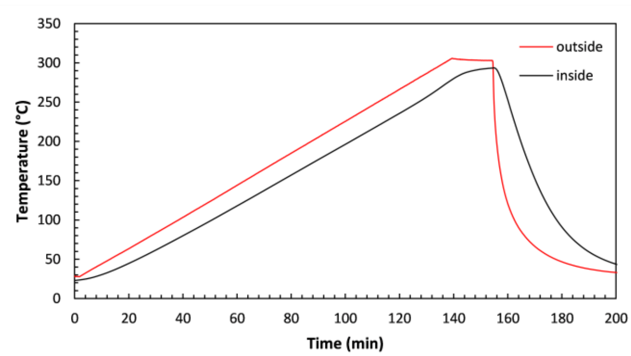

Fig. 1 Temperature profile of wood torrefied in Shimadzu reactor at 2 °C.min^{-1} till 300 °C for 15 min

of 32.25 wt% and 32.54 wt% respectively, possibly implying that the impregnation process had no impact on the wood structure. The mass loss gradually increased with the increase of potassium content in wood until reaching 7.49 wt% difference between 0.012 M (39.74 wt%) and the raw (32.25 wt%). The results are consistent with literature based on wood powder [11, 14–16].

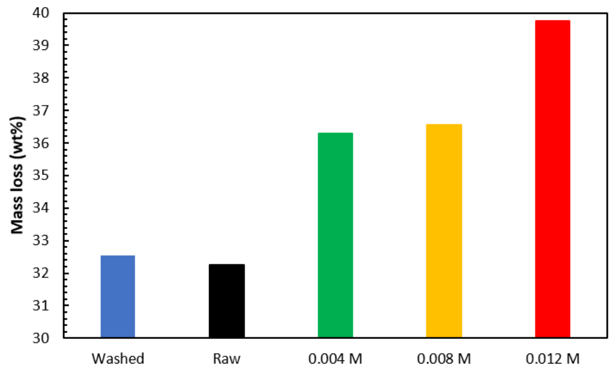

Fig. 2 Mass loss of wood after torrefaction at 300 °C for 15 min with different potassium concentrations

3.2 Color change

The change in color throughout the impregnation and the torrefaction processes is observed in Fig.3. The washing/impregnation process changed the color of wood (Tab.1) to a more yellow tone noticed by the increase of b* between the raw and the impregnated wood. This was probably due to the removal of water-soluble extractives that impact the wood's color [17].

Fig. 3 Color change of wood blocks with impregnation and torrefaction

Sample	*Untreated*			*Torrefied*			*ΔE*
	L*	a*	b*	L*	a*	b*	
Raw	54.52	6.01	12.63	29.81	2.20	1.53	27.38
Washed	54.98	8.99	21.94	26.90	2.22	1.16	35.60
0.004 M	55.99	8.62	21.33	26.95	2.16	0.97	36.05
0.008 M	56.46	7.90	20.42	26.72	1.67	0.62	36.33
0.012 M	53.22	8.10	19.83	26.21	2.05	0.92	33.57

Tab. 1 Colorimetry measurement on samples before and after torrefaction at 300 °C for 15 min

Moreover, the torrefaction efficiently rendered the wood darker (L*) with greener (a*) and bluer (b*) undertones. This change is due to many reactions such as byproducts formed from hemicelluloses degradation, oxidation, and cross-linking reactions [6]. The potassium itself had little effect on the change of colors. The impregnation procedure was responsible for the change in color observed by the increase of ΔE between raw and all other samples.

3.3 Higher heating value (HHV)

The HHV change with potassium addition and torrefaction is displayed in Fig. 4. The torrefaction had a large impact on the HHV that increased from 18.45 $MJ.kg^{-1}$ for untreated wood to 22.57 $MJ.kg^{-1}$ for the torrefied one. The HHV of the torrefied raw sample (22.57 $MJ.kg^{-1}$) was almost equal to that of the washed (22.48 $MJ.kg^{-1}$) validating that the impregnation procedure did not impact the wood's properties. The partial removal of extractives during K-impregnation had no noticeable effect on the HHV despite the literature stating that the extractives increase the HHV of wood [18]. It is speculated that in addition to the raw wood having more potassium, the procedure used for washing/impregnation led to the release of extractives having a lower HHV [19].

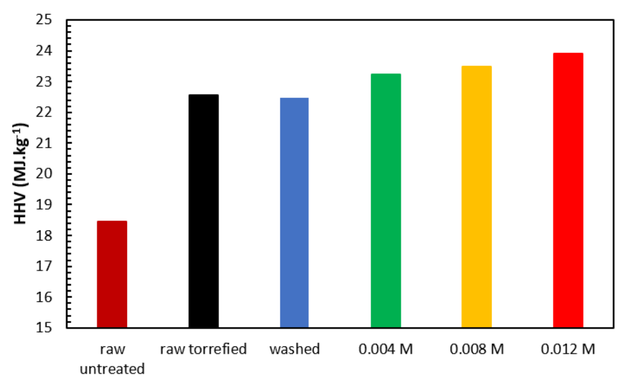

Fig. 4 HHV of wood with different potassium content before (raw untreated) and after torrefaction at 300 °C for 15 min

The highest HHV was achieved in the 0.012 M sample (23.9 $MJ.kg^{-1}$) thus increasing its energy by 29.54%. The increasing HHV with the torrefied K-impregnated wood, was probably attributed to the degradation of hemicelluloses and cellulose during torrefaction intensified by potassium addition [20]. This led to a relatively higher lignin fraction that has a higher HHV (23.3-26.6 $MJ.kg^{-1}$) indicating a better quality of the solid fuel produced. Moreover, the relative carbon content increases in the solid which increases the heating value [6,21].

4. CONCLUSION

In this study, wood blocks were impregnated with multiple solutions of K_2CO_3 having different concentrations and torrefied in an experimental reactor. The differences in mass loss between the samples were observed. The changes in color and heating value were analyzed using colorimeter and bomb calorimeter, respectively.

The impregnation process changes the wood's color probably with the removal of some extractives. The torrefaction darkens the samples when the hemicelluloses and part of the celluloses are degraded. The HHV of wood greatly increased with torrefaction and potassium content. Improving wood's calorific and physical properties with potassium, could help achieve carbon neutrality. More extensive tests were done but not presented in this abstract such as thermogravimetric analysis of torrefied wood (TGA), Elemental analysis to determine H/C and O/C ratios, XRD to study the effect of potassium and torrefaction on wood's crystallinity and ICP-AES to quantify the distribution of impregnated potassium in wood blocks.

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