

Influence of natural potassium content on the thermal treatment of woody biomass

LOPES QUIRINO Rafael¹, COLIN Baptiste¹, LIN Yu-Ying¹, PETRISSANS Anélie¹,
LECONTE François¹, CHEN Wei-Hsin³, PETRISSANS Mathieu¹

¹ Chemistry Department, Georgia Southern University, USA

² Université de Lorraine, Inra, LERMAB, F-88000 Epinal, France

³ Department of Aeronautics and Astronautics, National Cheng Kung University, Tainan, 701,
Taiwan

rquirino@georgiasouthern.edu

Key words: biomass; catalyst; potassium, pyrolysis; thermal treatment; torrefaction

Context and objectives

In order to lower the environmental impact of human activities, there has been a growing need for the development of value-added products from biomass. One of the main issues for the industrial use of biomass is the lack of consistency of the feedstock, which normally leads to products with uneven properties (da Silva et al., 2018). Carefully controlled heat treatment methods have been developed to enhance some properties of biomass. In such methods, the biomass is heated in the absence of oxygen (torrefaction), resulting in materials that can be more easily processed into more homogeneous products (da Silva et al., 2018). The torrefaction of woody biomass has shown several benefits for the preparation of materials for energy applications (Keeratiisariyakul et al., 2019). Despite the advancements made to date, key mechanism steps of torrefaction and pyrolysis of biomass aren't fully understood. There is indication that metals and metalloids naturally present in ligno-cellulosic biomass can catalyze its thermal degradation (Hwang et al., 2013; Shoulafar et al., 2016; Shen et al., 2020). The addition of potassium to biomass has been used as a means to improve the pyrolysis process (Hwang et al., 2013; Shen et al., 2020). The elucidation of the role of potassium during biomass thermal degradation enables the design of ideal heat treatment conditions for different biomass based on their natural potassium content. Tailored treatments to specific biomass resources ensure optimal and consistent properties of the final product, eradicating two of the major impediments for the widespread use of biomass at an industrial scale, which are their inherent variability and lack of consistent properties. It is widely accepted that a better control of time and temperature during biomass thermal treatment results in improvements in the quality, production cost, and environmental impact of the final products (Esteves and Pereira., 2009). Currently, the efficiency of biomass thermal treatment is compromised by a lack of fundamental knowledge of the chemical mechanisms involved in the process, including the role of potassium in these reactions. Treatment conditions are established, in most cases, by empiricism, often without taking into account initial wood properties, such as the natural potassium content. Tailored thermal treatment allows the strategic use of locally abundant, low cost biomass, adding value to natural resources for potential applications in energy, construction, and outdoor furniture.

To date, a number of studies have been published concerning the catalytic effects of impregnated potassium on thermal degradation of biomass. Natural potassium content still remains weakly known. In order to better understand the role of natural potassium during the thermal treatment of biomass, an unprecedented detailed investigation of the influence of

natural potassium content on the thermal treatment of different wood species has been carried out.

Material and methods

Thermogravimetric analysis was performed on two hardwood species (oak, *Quercus petraea* and beech, *Fagus sylvatica*) in inert (nitrogen) and oxidative (air) atmosphere: The natural potassium content of all species had been previously determined by ICP-AES. The thermodegradation behavior of all samples were analyzed by a thermogravimetric analyzer (TGA 2 (LF), Mettler Toledo). Prior to the experiments, the powdered woody samples were dried at 103 °C until mass stabilization. The samples were heated from 50 °C to 800 °C with a heating rate of 20 °C min⁻¹. The reaction gas flow was fixed at 100 mL min⁻¹.

Results and discussion

The latest results obtained indicate that potassium catalyzes the thermaloxidation of cellulose at higher temperatures (> 300°C). This can be observed by a comparison of DTG curves of samples of the same wood species (oak) bearing different concentrations of natural potassium and treated under air (Fig. 1). An equivalent correlation was also established using beech under the same conditions, but was impossible to be established when the treatment was conducted under inert atmosphere. Along the same lines, it was shown that lower treatment times can be achieved for the isothermal torrefaction of beech at 300 °C under inert atmosphere with a higher natural potassium concentration (Fig. 2). Further investigations include a detailed analysis of a broader selection of wood samples impregnated with specific amounts of potassium to complement and validate the data generated so far. Additionally, the contribution of other metals will be considered and evaluated appropriately.

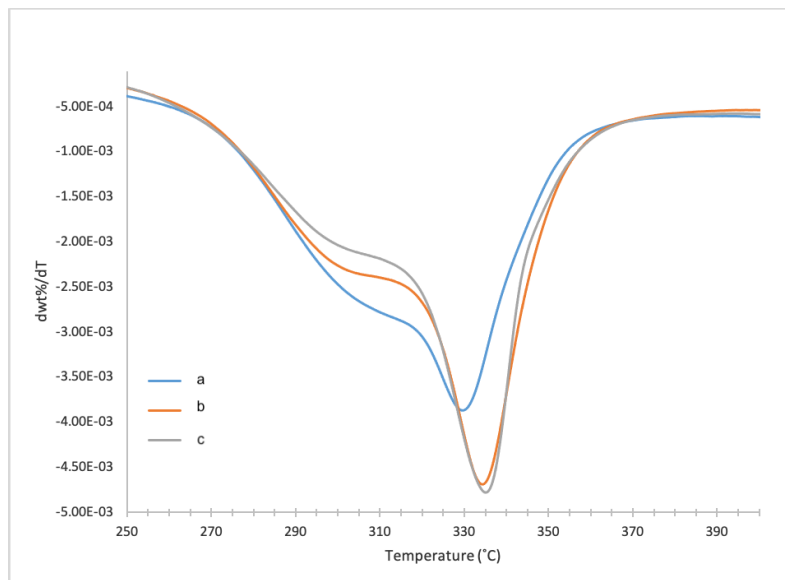


Fig. 1 : Derivative of thermogravitation curves (DTG) of oak samples heated from 50 °C to 800 °C at 20 °C/min under air. The concentration of natural potassium in the samples is as follows: (a) [K] = 0.1657%, (b) [K] = 0.1039%, and (c) [K] = 0.0707%.

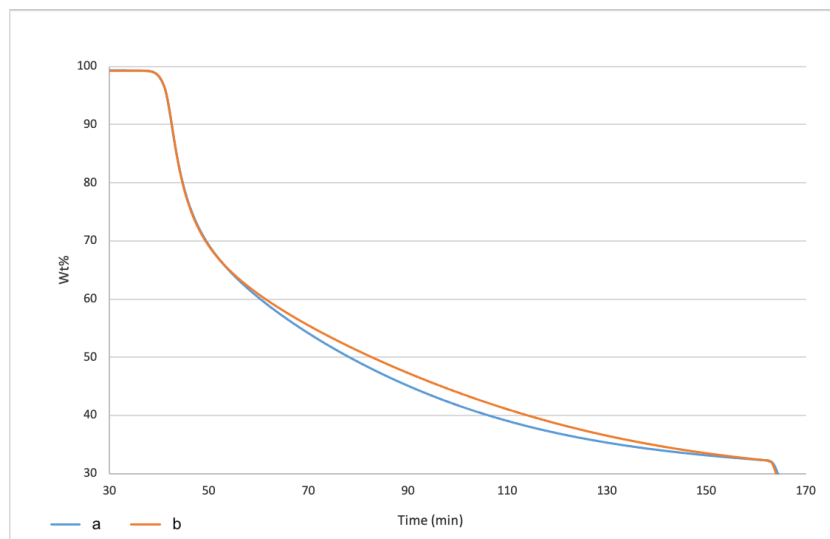


Fig. 2 : Thermogravimetric curves of beech samples treated at 300 °C under N₂.
The concentration of natural potassium in the samples is as follows:
(a) [K] = 0.2047% and (b) [K] = 0.1274%.

Conclusion remarks and perspectives

The results presented herein constitute an encouraging contribution towards a better understanding of the influence of natural mineral content in the thermal treatment of biomass. Elucidation of catalytic processes during biomass pyrolysis and/or torrefaction allows for better control of treatment duration, and quality and homogeneity of the product. Such control is achieved by:

- taking into account the natural potassium content of the wood biomass when determining treatment time;
- developing a selection method for the wood species with a high and consistent potassium content to decrease treatment time.

Acknowledgements

This material is based upon research partially supported by the Thomas Jefferson Fund of the Embassy of France in the United States and the FACE Foundation. The authors would also like to thank Georgia Southern University and the University of Lorraine for financial support.

References

- da Silva C.M.S., Carneiro A. de C.O., Vita, B.R., Figueiró C.G., Fialho L. de F., de Magalhães M.A., Carvalho A.G., Cândido W.L. (2018) Biomass torrefaction for energy purposes – Definitions and an overview of challenges and opportunities in Brazil. *Renewable and Sustainable Energy Reviews* 82, 2426–2432. <https://doi.org/10.1016/j.rser.2017.08.095>
- Keeratiisariyakul P., Rousset P., Pattiya A. (2019) Coupled effect of torrefaction and densification pre-treatment on biomass energetic and physical properties 10.
- Hwang H., Oh S., Cho T.-S., Choi I.-G., Choi J.W. (2013) Fast Pyrolysis of Potassium Impregnated Poplar Wood and Characterization of Its Influence on the Formation as Well as Properties of Pyrolytic Products. *Bioresource Technology* 150, 359–366. <https://doi.org/10.1016/j.biortech.2013.09.132>.

Shoulaifar T.K., DeMartini N., Karlström O., Hupa M. (2016) Impact of Organically Bonded Potassium on Torrefaction: Part 1. Experimental. Fuel, 165, 544–552. <https://doi.org/10.1016/j.fuel.2015.06.024>.

Shen Y., Zhang N., Zhang S. (2020) Catalytic Pyrolysis of Biomass with Potassium Compounds for Co-Production of High-Quality Biofuels and Porous Carbons. Energy, 190, 116431. <https://doi.org/10.1016/j.energy.2019.116431>.

Esteves B.M., Pereira H.M. (2009) Wood Modification by Heat Treatment: A Review. Bioresources, 4(1), 370-404.