# PYROLYSIS OF LARGE WOOD PARTICLES: KINETIC MODELING AND EXPERIMENTAL VALIDATION

**Million M. Afessa[1,2], A.Venkata Ramayya[1], Andrea Locaspi[2], Paulo Debiagi[3], Alessio Frassoldati[2], Tiziano Faravelli[2], Anna Szepannek[4,5], Angela Hofmann[4], Christoph Pfeifer[5]**

E-mail: millionmerid208@gmail.com /million.merid@ju.edu.et
[1] Faculty of Mechanical Engineering, Jimma Institute of Technology, JiT, Ethiopia
[2] Department of Chemistry, Materials and Chemical Engineering, Politecnico di Milano
[3] Institute for Simulation of Reactive Thermo-Fluid Systems, TU Darmstadt, Germany
[4] Josef Ressel Centre for the Production of Powdered Activated Carbon from Municipal Residues, Innsbruck, Austria
[5] Institute of Chemical and Energy Engineering, Department of Material Sciences and Process Engineering, University of Natural Resources and Life Sciences, Vienna, Austria

## Abstract

The pyrolysis of large wood particles, which has a substantial impact in characterizing the pyrolysis process, is the focus of this research. This study provides new experimental data for cubic wood thick particles. The experimental setup was designed mainly to investigate the effect of heat and mass transfer limitations on the decomposition rate of a single biomass particle. Experimental results are compared with 1D modeling results to comprehend the pyrolysis characteristics, aiming at a further validation of a comprehensive mathematical modeling of thermochemical biomass conversion. The results suggest that a 1D model, which assumes an equivalent spherical geometry, can accurately capture the temperature profile at the surface and to an acceptable level at the core of the particle. Likewise, the model results can capture the behavior of exothermic phenomena observed in the experiments. The degree of pyrolysis, i.e. the extent to which the particles pyrolyzed under various scenarios is also correctly predicted. Modest differences in prediction are due to simplifications in particle geometry and chemical composition of biomass samples. These study findings are valuable for understanding pyrolysis of large wood particles and improving the design of efficient conversion technologies.

## 1. Introduction

Biomass has been widely recognized and exploited as a renewable energy source for decades, and it is now seen as a worthwhile alternative to fossil fuels. Thermochemical processes decompose the complex biomass structure into simpler molecular compounds[1]. Biomass pyrolysis which is a precursor of other thermochemical processes such as gasification, produces solid, gas, and liquid phases[2]. Despite significant progress, this technology has not been commercially effective for large

applications, owing to heat and mass transfer limitations within the pyrolyzing particles [3].

Reducing the sizes of particles to kinetically controlled sizes is one approach to improve heat and mass transfer limitations [4]. However, it increases the processing time and energy demand, and thus it may not be realistic for large-scale applications [5]. Conversely, pyrolysis of relatively large particles using microwave-assisted pyrolysis at lower temperature has been reported to improve heat and mass transfer efficiency [6]. Nevertheless, temperature profiles and reaction extents are highly non-uniform in large particles, rendering pyrolysis a challenging process. In this regard, significant efforts were made to characterize temperature profiles inside large biomass particles [4]. Both endothermic and exothermic phenomena were observed during the pyrolysis of thick particles[7]. It was also revealed experimentally that the endothermicity prevails at low conversion stages [8], whereas exothermic reactions become important at higher conversion rate [9].

Particle model simulations have been also used to study intraparticle transport in larger particles, but the complexity of the simulation varies depending on the kinetic schemes, numerical approaches, and phenomena under consideration. Larger particle sizes, in general, increase modeling complexity[1]. Spherical, cylindrical, and slab-shaped particles have previously been studied through the use of modeling and experimental methods [9]. On thermally thick particles, there are indeed few experimental studies and mathematical modeling in the literature. The new experiment presented in this work represents an effort to provide new data for different kind of wood particles. These experiments constitute a useful dataset to further validate and improve a comprehensive mathematical model of thermochemical biomass conversion. The particle-scale model handles both kinetics and transport phenomena, thus it is able to predict the temporal and spatial evolution of composition and temperature inside the particle.

Accordingly, the objective of this paper is to investigate the pyrolysis characteristics of cubic wood particles in slow pyrolysis conditions, i.e. temperatures of 300, 375, and 450 $^{o}$C. This work is also to further evaluate the performances of the 1-D model framework, called BioSMOKE++ developed by the CRECK group at Politecnico di Milano, adopting the recently improved kinetic scheme. The findings contribute to a better understanding on the significance of geometric simplification during 1-D model simulation, as well as implications of transforming a cubic particle (of 3 cm) into an equivalent sphere to predict endothermic and exothermic events in pyrolyzing particles.

## 2. Experimental Methods

The aim of the present experiment campaign is to determine pyrolysis properties of two types of waste wood and fresh wood from the same species when allothermically pyrolyzed under the defined conditions. The considered materials are spruce (bulk density = 540 kg/m$^3$) and larch (bulk density = 600 kg/m$^3$).

### 2.1. Biomass samples and Characterization

The examined types of wood are commonly used in Austria, and for each one waste wood and the respective fresh wood are considered for comparison. Waste wood is the one exposed to external influences and mechanically and/or biologically weathered over the years. Fresh wood is the one that has already been chopped but has not been exposed to long-term external influences. The ultimate analysis and the established empirical correlations proposed by Debiagi et al. [10] are adopted. Further work will address investigating the real biochemical com position of the biomass samples.

### 2.2. Experimental setup and procedures

Pyrolysis temperatures ($T_{set}$) are 300°C, 375°C, 450°C. Thermocouples (Type K, diameter 1mm) are led into the bottom of a pyrolysis box and fixated. Holes (diameter 1,2mm, length 1,5cm) are drilled in the center of the cross section of the cubes, perpendicular to direction of growth. The cubes are then placed directly on the thermocouples. The box is put into a muffel oven (L 15/11/B410, Nabertherm, 3,5 kW max. power) at ambient temperature, where nitrogen is led into (flowrate 1L/min). The oven is heated to $T_{set}$ in 30 min and kept at $T_{set}$ for 90 min. The box then cools down in the oven. T thermocouples are led outside the box and oven, where data is recorded via a thermologger (BTM-420 SC, LT Lutron). For each temperature and wood source four samples are pyrolyzed and results are averaged.
All wood and charcoal samples are ground, using a granulator (Pulverisette 25, Fritsch) and a centrifugal mill (ZM 200, Retsch) to reach particle size <1mm. Degree of pyrolysis and volatile content are determined via thermogravimetric analysis TGA (STA 449 F5 Jupiter, Netsch, Autosampler/ 19 samples per run). 10-20mg of particles are weighed as the initial mass. TGA segments are I (25°C-110°C, 15°C/min, $N_2$) and II (110°C for 10 min, $N_2$) to determine moisture content, III 110°C-900°C, 30°C/min, $N_2$) and IV (900°C for 12 min, $N_2$) to determine volatile content ($\omega_{\mathrm{vol,c}}$ for charcoal, $\omega_{\mathrm{vol,w}}$ for wood), V (900°C, for 12 min, synthetic air) to determine ash content. Total carbon, hydrogen and nitrogen content is determined via CHN analysis (TruSpec CHN, Leco), with an initial mass of 100-200mg. Samples are analysed twice and the results are averaged. Degree of pyrolysis η is calculated via equation (Eq.1).

$$\eta = 100 \cdot \left(1 - \frac{\omega_{vol,c}}{\omega_{vol,w}}\right) \qquad (1)$$

### 2.3. Description of the models

The recently revised CRECK-S-B kinetic model proposes a more comprehensive way to describe the kinetics of biomass pyrolysis. In this model, complex structure and composition of biomasses are lumped into a few reference components that

represent the most common components found in biomass feedstock. The detailed multistep pyrolysis scheme going to be applied in this work is based on the one originally developed by [11]and modified in the later stage by [10]. This scheme contains 32 reactions with 58 species (29 volatiles and 29 solid species) and is coupled to a 1-D particle model called the BioSMOKE++_1D. The model solves heat and mass balance equations on a 1D computational grid for both the gas and solid (porous) phase [12].

## 3. Results and Discussion

**Figure 1** shows a comparison between experimental results and predicted temperature profiles at the surface and centre of the particle for three pyrolysis temperatures and for larch wood (old (LA) & fresh (LF)).

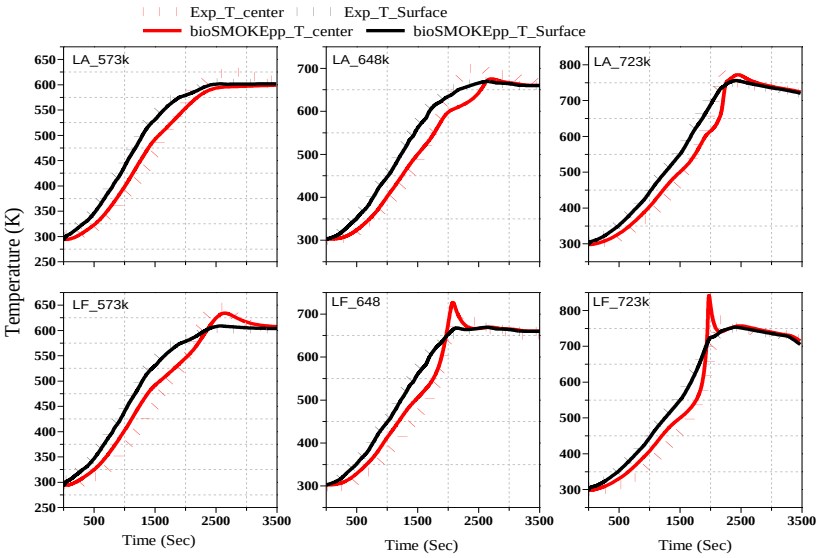


**Figure 1.** Temperature profiles of the particle compared with simulation for a 3x3x3 $cm^3$ wood particle modelled as sphere with the same surface area at r = 0 (red) and r = R (black) at three pyrolysis temperatures (300, 375 and 450 °C)

The result shows that temperature in the center can exceed the temperatures measured on the surface of the particles as a result of the exothermic clarification reactions occurring inside the particles. These trends were also encountered in other available studies in literature [13]. The results indicate that a difference in the relative composition of wood in terms of its components (Cellulose, lignin and hemicelluloses) varies widely within species and even within the same tree. Cellulose, lignin and hemicelluloses each have different onset temperatures at which

they degrade. Thus, the biomass composition is a major factor influencing the behaviour of the particle with regard to exothermicity. The anisotropic properties of the particles can influence the pyrolysis behaviour. Therefore, characterization of the chemical composition of the biomass and the adoption of a 3D model, able to account for anisotropic effects would further improve the results. Nevertheless, Figure 1 shows that model predictions agree well with experimental measurements. The model is able to predict the effect of pyrolysis temperature and wood type (LA, LF) on the extent of the exothermic effects.

Model predictions were also compared to the experimentally measured degree of pyrolysis. Figure 2 show that the model can capture the effect of temperature on degree of pyrolysis. On the contrary the model is not able to predict the effect of wood type. This discrepancy is attributed to the assumptions made during numerical simulations, particularly the estimated chemical composition of the biomass and of thermal conductivity of the biomass samples.

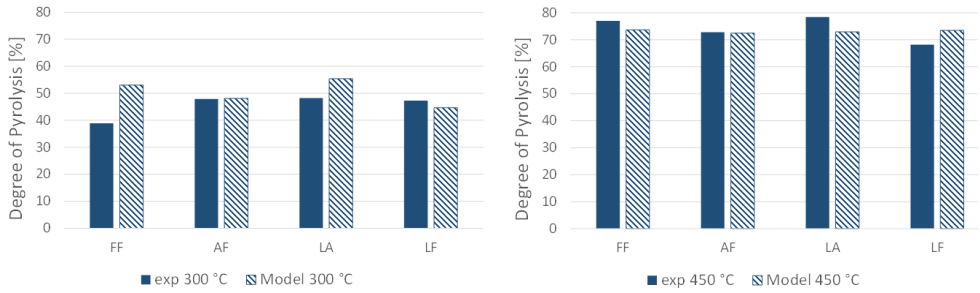


**Figure 2.** Effect of pyrolysis temperature on degree of pyrolysis for different wood particles. Comparison between experimental measurements and model predictions.

## 4. Conclusion and Future insights

This work provides new experimental data on the pyrolysis of thick biomass particles of different wood cubes. It also shows that the CRECK kinetic model of biomass pyrolysis, coupled to a simple 1D model for thick particle, is able to replicate the over-shooting of the center temperature of thick particles, while also reasonably predicting the effect of temperature on the degree of pyrolysis for different wood particles. The comparison of experimental and model results has provided insights into the mechanisms and kinetics of biomass pyrolysis, highlighting the importance of parameters such as particle size, geometry, and biomass composition in determining pyrolysis characteristics and biomass pyrolysis product distribution. Further work will be done in the future to extend the experimental dataset, including biomass composition, and to improve the model by including anisotropic effects which cannot be accounted for by the1D model.

## Acknowledgements

This study at Politecnico was conducted within the Agritech National Research Center and received funding from the European Union Next-GenerationEU (PNRR) – M4, C2, I1.4, D.D. 1032 17/06/2022, CN00000022). This manuscript reflects only the authors' views and opinions; neither the EU nor the EU Commission can be considered responsible for them.

## References

[1] G. Gauthier "Pyrolysis of Thick Biomass Particles: Experimental and Kinetic Modelling," *Chem. Eng. Trans.*, vol. 32, pp. 601–606, Jun. 2013, doi: 10.3303/CET1332101.

[2] A. Garba, *Biomass Conversion Technologies for Bioenergy Generation: An Introduction*. IntechOpen, 2020. doi: 10.5772/intechopen.93669.

[3] M. Van de Velden, J. Baeyens, A. Brems, B. Janssens, and R. Dewil, "Fundamentals, kinetics and endothermicity of the biomass pyrolysis reaction," *Renew. Energy*, vol. 35, no. 1, pp. 232–242, Jan. 2010, doi: 10.1016/j.renene.2009.04.019.

[4] H. Bennadji, K. Smith, M. J. Serapiglia, and E. M. Fisher, "Effect of Particle Size on Low-Temperature Pyrolysis of Woody Biomass," *Energy Fuels*, vol. 28, no. 12, pp. 7527–7537, Dec. 2014, doi: 10.1021/ef501869e.

[5] X. Shi, J. Gao, and X. Lan, "Modeling the Pyrolysis of a Centimeter-Sized Biomass Particle," *Chem. Eng. Technol.*, vol. 42, no. 12, pp. 2574–2579, 2019, doi: 10.1002/ceat.201900085.

[6] M. M. Hasan, X. Hu, R. Gunawan, and C.-Z. Li, "Pyrolysis of large mallee wood particles: Temperature gradients within a pyrolysing particle and effects of moisture content," *Fuel Process. Technol.*, vol. 158, pp. 163–171, Apr. 2017, doi: 10.1016/j.fuproc.2016.12.018.

[7] W. C. Park, A. Atreya, and H. R. Baum, "Experimental and theoretical investigation of heat and mass transfer processes during wood pyrolysis," *Combust. Flame*, vol. 157, no. 3, pp. 481–494, Mar. 2010, doi: 10.1016/j.combustflame.2009.10.006.

[8] C. A. Koufopanos, N. Papayannakos, G. Maschio, and A. Lucchesi, "Modelling of the pyrolysis of biomass particles. Studies on kinetics, thermal and heat transfer effects," *Can. J. Chem. Eng.*, vol. 69, no. 4, pp. 907–915, 1991, doi: 10.1002/cjce.5450690413.

[9] S. Vikram, P. Rosha, and S. Kumar, "Recent Modeling Approaches to Biomass Pyrolysis: A Review," *Energy Fuels*, vol. 35, no. 9, pp. 7406–7433, May 2021, doi: 10.1021/acs.energyfuels.1c00251.

[10] P. Debiagi, G. Gentile, A. Cuoci, A. Frassoldati, E. Ranzi, and T. Faravelli, "A predictive model of biochar formation and characterization," *J. Anal. Appl. Pyrolysis*, vol. 134, pp. 326–335, Sep. 2018, doi: 10.1016/j.jaap.2018.06.022.

[11] E. Ranzi "Chemical Kinetics of Biomass Pyrolysis," *Energy Fuels*, vol. 22, no. 6, pp. 4292–4300, Nov. 2008, doi: 10.1021/ef800551t.

[12] G. Gentile, A. Cuoci, A. Frassoldati, T. Faravelli, and E. Ranzi, "A Comprehensive CFD Model for the Biomass Pyrolysis," *Chem. Eng. Trans.*, vol. 43, pp. 445–450, May 2015, doi: 10.3303/CET1543075.

[13] M. Corbetta "Pyrolysis of Centimeter-Scale Woody Biomass Particles: Kinetic Modeling and Experimental Validation," *Energy Fuels*, vol. 28, no. 6, pp. 3884–3898, Jun. 2014, doi: 10.1021/ef500525v.