University of Belgrade
Technical Faculty in Bor
Mining and Metallurgy
Institute Bor

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Editors:
Ljubiša Balanović
Dejan Tanikić

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PREFACE

On behalf of the Organizing Committee, it is a great honor and pleasure to welcome all esteemed participants of the **56th International October Conference on Mining and Metallurgy (IOC 2025)**, scheduled to take place at **Bor Lake, Serbia**, from **October 22nd to 25th, 2025**.

The collaborative efforts of the University of Belgrade – Technical Faculty in Bor and the Mining and Metallurgy Institute Bor have once again brought together academia, industry, and research institutions to organize this year's IOC. Our focus remains firmly set on presenting the latest research achievements and technological advancements in geology, mining, metallurgy, materials science, technology, environmental protection, and other engineering disciplines.

This year's conference program is rich and diverse, featuring **4 plenary lectures, 4 invited lectures, 158 full papers, and 6 abstracts**. The proceedings reflect the contributions of authors from **19 countries**: Austria, Bosnia and Herzegovina, Bulgaria, Canada, China, Croatia, Germany, Hungary, India, Mexico, Montenegro, Poland, Romania, Russia, Serbia, Slovakia, Slovenia, Turkey, and the United Kingdom. Among the submitted papers, eight young researchers under the age of 35 have qualified to participate in the "**MDPI Young Researcher Award**" competition, further emphasizing the conference's commitment to supporting and recognizing excellence among the new generation of scientists and engineers.

We are also delighted to host the **9th International Student Conference on Technical Sciences (ISC 2025)**, running in parallel with IOC 2025. The student conference brings together young researchers from Serbia and the wider region, with **one plenary** and **50 student papers** presented, offering an invaluable opportunity for the next generation of scientists and engineers to share their ideas and discuss the future of their disciplines with experts. The "**Professor Dragana Živković Best Student Paper Award**" will be presented to the most outstanding student contribution based on originality, research quality, and presentation.

The Organizing Committee expresses its deepest gratitude to all who have supported this event. Our General Sponsor is the Ministry of Science, Technological Development, and Innovation of the Republic of Serbia. We are especially grateful to our Platinum Donors, HBIS Serbia and Serbia Zijin Mining, as well as our Gold Sponsor, DPM Metals Inc., and our Gold Donors, Copper Mill Sevojno and Serbia Zijin Copper Bor. This year, the conference is also supported by the Silver Donor, "MC LABOR" d.o.o. Beograd.

We proudly host a diverse exhibition, featuring Indemak, Labtim SE d.o.o., MERIS d.o.o., Krug International LTD, Altium International d.o.o., Metalurg Foundry Ltd., Fugro Germany Land GmbH, Analysis d.o.o., Lola institut, Tescan and Mikrolux d.o.o., Trokuttest Serbia, Novos d.o.o., Changsha Rui Rui Technology Co., Ltd., MDPI and the Winery of Bukovo Monastery. The official opening of the conference has been supported by Epiroc Srbija a.d.. Finally, we warmly acknowledge our Friends of the Conference: Messer Tehnogas AD Belgrade, the China-Serbia Joint Laboratory on Green Steel Manufacturing, and the Foundation B.Sc. Boško Injac.

We sincerely thank all authors, committees, reviewers, speakers, and chairpersons for their invaluable contributions to shaping IOC 2025. We are confident that the conference will once again serve as a alive platform for scientific exchange, professional networking, and the promotion of sustainable development in mining, metallurgy, and related fields.

On behalf of the 56th IOC Organizing Committee,
Prof. dr Ljubiša Balanović

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KINETIC MODELING OF OAK WOOD THERMAL DEGRADATION USING THE DISTRIBUTED ACTIVATION ENERGY MODEL (DAEM)

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Abstract
This study investigates the thermal degradation behavior of oak wood using non-isothermal thermogravimetric analysis (TGA) under inert conditions. The Distributed Activation Energy Model (DAEM) was applied to model the pyrolysis kinetics, capturing the complex decomposition of lignocellulosic components. The pre-exponential factor, mean activation energy, and standard deviation were determined by fitting the DAEM to experimental data. The model showed excellent agreement with the observed TGA curve, achieving a high coefficient of determination ($R^2 = 0.9834$). The results highlight the dominance of hemicellulose degradation in early pyrolysis stages and demonstrate the suitability of DAEM for representing the thermal behavior of hardwood biomass. The derived kinetic parameters offer valuable input for reactor design and simulation in bioenergy applications.

***Keywords**: oak wood, pyrolysis, thermal degradation, DAEM, kinetic modeling, TGA*

1. INTRODUCTION

The increasing demand for renewable energy sources has positioned biomass, such as oak wood, as a critical component in the transition towards a sustainable energy future. Thermochemical conversion processes, including pyrolysis, gasification, and combustion, are the primary pathways for transforming this solid feedstock into valuable energy and chemical products. The design, optimization, and scaling of reactors for these processes depend fundamentally on a precise understanding of the material's thermal degradation behavior. In this context, kinetic studies are indispensable, as they provide the essential parameters (activation energy and pre-exponential factor) that quantify the reaction rates governing the decomposition process. These parameters serve as vital inputs for robust process modeling and simulation. However, modeling the kinetics of biomass is challenging. Oak wood is a heterogeneous composite of hemicellulose, cellulose, and lignin, each degrading through complex and overlapping reactions over a wide temperature range. Consequently, simpler kinetic approaches are often not adequate. Model-fitting methods, for example, which assume a single reaction mechanism for the entire process, are a significant oversimplification that can yield parameters with limited physical meaning. Model-free (isoconversional) methods, such as the Ozawa-Flynn-Wall (OFW) [1,2] and Kissinger-Akahira-Sunose (KAS) [3,4] models, represent an improvement as they do not assume a reaction model and can show how the effective activation energy varies with the extent of conversion. Despite this advantage, they typically do not provide a complete kinetic model capable of accurately reconstructing the original experimental data from the derived parameters. The Distributed Activation Energy Model (DAEM) provides a more physically realistic and powerful framework. DAEM presumes that the complex overall reaction is a superposition of countless independent, parallel, first-order reactions, where the activation energies are not a single value but follow a statistical distribution, typically Gaussian [5]. This approach elegantly captures the energetic

heterogeneity of the biomass components. The primary merit of DAEM is that it yields a complete and compact "kinetic triplet" (the pre-exponential factor (A), the mean activation energy (E_0), and the standard deviation of the distribution (σ)). This triplet constitutes a full kinetic model that can be used to accurately predict the material's degradation behavior, offering a robust method for model validation [6]

Therefore, the aim of this study is to apply the DAEM to non-isothermal thermogravimetric analysis (TGA) data to determine the complete kinetic triplet for the pyrolysis of oak wood and to validate the model's accuracy in describing its complex thermal degradation process.

2. EXPERIMENTAL

2.1 Material and Thermogravimetric Analysis (TGA)

The feedstock material used in this study was oak wood (Quercus sp.). The sample was prepared by drying at 105°C for 24 hours to remove moisture, then milling and sieving to obtain a particle size fraction of < 100 μm.

The thermal degradation behavior of the oak wood sample was investigated using a Perkin Elmer TGA 4000 (Norwalk, CT, USA). A sample mass of approximately 10 mg was placed in a ceramic crucible. The analysis was conducted under a nitrogen atmosphere with a constant flow rate of 20 mL/min to ensure an inert environment and prevent thermo-oxidative degradation. The sample was heated from 30°C to 900°C at a constant heating rate (β) of 5°C/min. The instrument recorded the sample mass as a function of time and temperature. The resulting data provides the basis for the kinetic analysis.

2.2 Kinetic Modeling: The Distributed Activation Energy Model (DAEM)

To describe the complex kinetics of oak wood pyrolysis, the Distributed Activation Energy Model (DAEM) was employed. The thermal degradation of lignocellulosic biomass, such as oak wood, is not a single-step reaction. It is a complex process involving the simultaneous and overlapping decomposition of its primary components: hemicellulose, cellulose, and lignin. Each of these components degrades through a multitude of chemical reactions. Simpler kinetic models, like single-step model-fitting methods, fail to capture this inherent complexity and can lead to kinetic parameters that lack true physical meaning. The DAEM provides a more physically realistic framework by assuming that the overall pyrolysis process consists of an infinite number of independent, parallel, first-order reactions. Each of these reactions is characterized by its own activation energy, E. The central concept of DAEM is that these activation energies are not discrete values but are continuously distributed around a mean value, following a statistical probability distribution function, $f(E)$. The overall conversion rate at any given time or temperature is the sum of the rates of all these individual reactions. The rate of a single first-order reaction can be described by the Arrhenius equation:

$$\frac{d\alpha}{dt} = A \cdot \exp\left(-\frac{E}{RT}\right) \cdot (1-\alpha)$$

where: α is the conversion fraction; t is time (s); A is the pre-exponential factor (s^{-1}); E is the activation energy (J/mol); R is the universal gas constant (8.314 J/mol·K) and T is the absolute temperature (K).

The conversion, α, is defined based on the mass loss measured during TGA:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f}$$

where m_0, m_t, and m_f are the initial, instantaneous, and final mass of the sample, respectively.

Derivation expressed here follow exposition provided in [5]. For a non-isothermal process with a constant heating rate, $\beta = dT/dt$, the rate equation can be integrated to find the conversion for a single reaction with activation energy E:

$$1 - \alpha(T, E) = \exp\left(-\frac{A}{\beta}\int_{T_0}^{T} \exp\left(-\frac{E}{RT'}\right) dT'\right)$$

To obtain the total conversion for the entire material, this expression is integrated over the distribution of activation energies, $f(E)$:

$$1 - \alpha(T) = \int_0^{\infty} \exp\left(-\frac{A}{\beta}\int_{T_0}^{T} \exp\left(-\frac{E}{RT'}\right) dT'\right) \cdot f(E) dE$$

It is commonly assumed, and has been shown to be effective for biomass, that the activation energies follow a Gaussian distribution:

$$f(E) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(E - E_0)^2}{2\sigma^2}\right)$$

This distribution is defined by two key parameters: the mean activation energy (E_0) and the standard deviation (σ). The standard deviation, σ, represents the width of the distribution and is an indicator of the energetic heterogeneity of the reacting components. A larger σ value implies a more complex material with a wider range of simultaneous reactions. The goal of the DAEM analysis is to determine the three kinetic parameters (A, E_0, and σ) that best describe the experimental TGA data. This "kinetic triplet" provides a complete and physically meaningful description of the thermal degradation process. In this work, the kinetic triplet was determined by fitting the DAEM equation to the experimental TGA data using a non-linear least-squares optimization algorithm implemented in Python. The algorithm minimizes the sum of the squared differences between the experimental conversion values (α_{exp}) and the model-predicted values (α_{pred}).

3. RESULTS AND DISCUSSION

The thermal decomposition of the oak wood sample under an inert nitrogen atmosphere was investigated using thermogravimetric analysis (TGA) and its derivative (DTG) curve. Figure 1 shows the TG and DTG curves, which represent the percentage of mass loss and the corresponding mass loss rate as functions of temperature. An initial mass loss of approximately 3% below 100 °C corresponds to moisture evaporation and the release of light volatiles. This is followed by a major decomposition stage between 235 and 360 °C, attributed to the breakdown of structural polymers. Above 360 °C, mass loss continues at a slower rate due to the pyrolysis of more stable compounds, resulting in approximately 11% char residue at 900 °C. The DTG curve exhibits a sharp peak around 355 °C (cellulose degradation), a shoulder near 285 °C (hemicellulose), and a broad tail above 400 °C (lignin), reflecting the complex nature of lignocellulosic pyrolysis. Hemicellulose decomposes first, overlapping with cellulose, while lignin degrades gradually starting around 200 °C. Cellulose and hemicellulose primarily contribute to volatile product formation, whereas lignin is mainly responsible for char production [7].

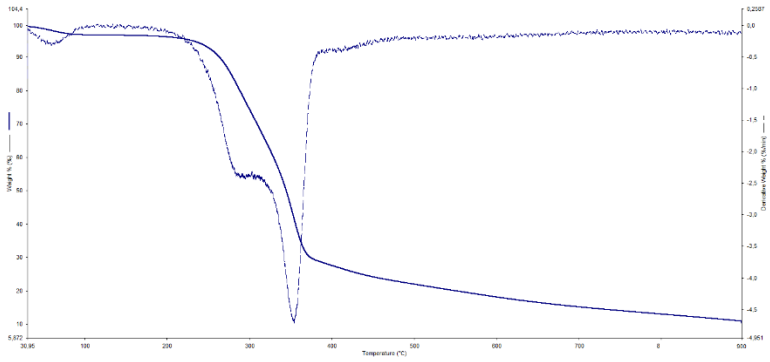

Figure 1. Thermogravimetric (TG, solid line) and derivative thermogravimetric (DTG, dashed line) curves of oak tree biomass obtained during thermal analysis in an inert nitrogen atmosphere at a heating rate of 5 °C/min.

The experimental data was fitted to the Distributed Activation Energy Model (DAEM) to obtain a comprehensive kinetic description of the pyrolysis process. The obtained kinetic parameters are: Pre-exponential Factor (A): 1.00×10^{8} s^{-1}; Mean Activation Energy (E_0): 131.23 kJ/mol and Standard Deviation (σ): 15.64 kJ/mol. The model yielded a coefficient of determination (R^2) of 0.9834, indicating a strong correlation between the experimental data and the DAEM-predicted curve, confirming the model's suitability for describing the overall process. The mean activation energy (E_0) of 131.23 kJ/mol is a particularly interesting result. This value is lower than the overall activation energy typically reported for the bulk pyrolysis of hardwoods, which often falls in the 170-200 kJ/mol range [6,8]. However, it is highly characteristic of the thermal degradation of hemicellulose. This suggests that the DAEM fit, while modeling the entire conversion curve, has identified the initial, lower-temperature decomposition of hemicellulose as the dominant energetic barrier controlling the onset and early stages of pyrolysis for this oak wood sample. The pre-exponential factor (A) is correspondingly lower than many values reported for bulk biomass pyrolysis. This is consistent with the kinetic compensation effect, a phenomenon where a lower activation energy is mathematically compensated by a lower pre-exponential factor to describe a given reaction rate. The combination of a lower E_0 and A accurately models the observed reaction, particularly in the crucial low-temperature regime. The standard deviation (σ) of 15.64 kJ/mol quantifies the width of the energy distribution. This value reflects the inherent heterogeneity of the material, accounting for the overlapping reactions of not just hemicellulose, but also the initial stages of cellulose and lignin degradation that occur within this energetic spectrum. The robustness of the derived kinetic triplet was validated by comparing the TGA curve predicted by the model against the experimental data across the entire temperature range. As shown in Figure 2, the DAEM curve closely follows the experimental data in the main pyrolysis region but slightly deviates above 400 C, where the model predicts a faster decline than observed experimentally.

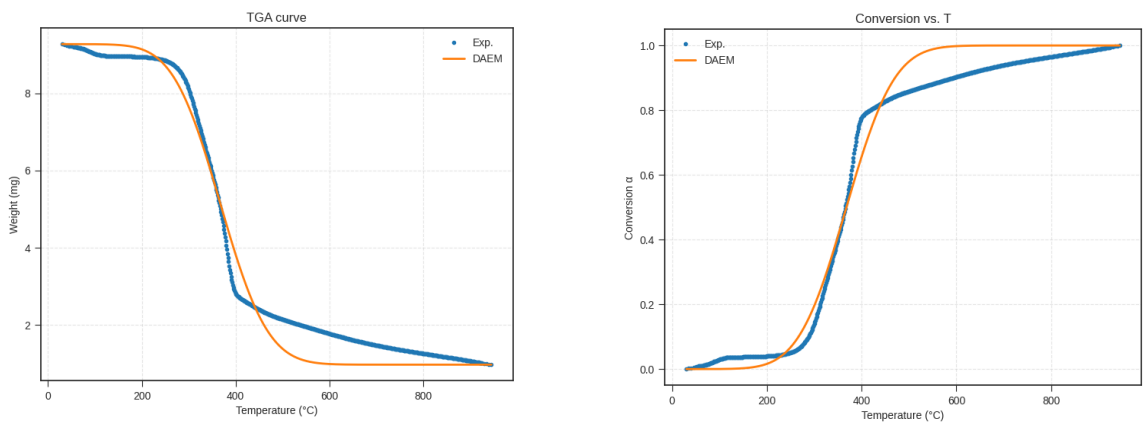

Figure 2. Weight lost curve (left) and conversion profile (right) for oak wood pyrolysis, illustrating model accuracy (experimental TGA curve (blue) and DAEM fit (orange))

The successful application of the DAEM provides a reliable kinetic model for oak wood pyrolysis. The obtained kinetic triplet serves as a compact and physically meaningful tool for predicting the material's thermal behavior.

Obtained DAEM parameters reveal that the oak sample was energetically easy to decompose, as its transformation during the early pyrolysis phase was largely influenced by less energetic routes. The main devolatilization window (ca. 235–360 °C) with a DTG peak near 355 °C and a lower-temperature shoulder around 285 °C aligns with hemicellulose–cellulose overlap. Residual char of ≈11% at 900 °C also falls in the expected hardwood range. To compare our results with those from the literature, we referred to an international round-robin study on beech wood [6]. That study, which fitted three parallel reactions (cellulose, hemicellulose, lignin), reported component activation energies of approximately 150 kJ mol^{-1} for hemicellulose and ca. 180 kJ mol^{-1} for cellulose. The standard deviations were moderate (ca. 8–15 kJ mol^{-1}), while lignin showed markedly higher and less stable values at high conversion. Cai et al. used a three-parallel DAEM and found peaks centered near 178 kJ mol^{-1} (xylan) and 210 kJ mol^{-1} (cellulose), with narrow σ for cellulose and broader distributions for lignin, reflecting component heterogeneity [8]. Taken together, our single-Gaussian E_0 = 131 kJ mol^{-1} is lower than the component-wise DAEM means commonly reported for hardwoods. This can be attributed to the model fit being most constrained by the initial, dominant mass loss from low-energy hemicellulose pathways, which are averaged with less-emphasized, high-temperature reactions in the single-distribution DAEM.

4. CONCLUSION

This study applied the Distributed Activation Energy Model (DAEM) to non-isothermal TGA of oak wood (Quercus sp.) and produced a compact kinetic triplet (A, E_0, σ) that accurately reconstructed the experimental TG curve. The parameters ($A = 1.00 \times 10^8$ s^{-1}, E_0 = 131.23 kJ mol^{-1}, σ = 15.64 kJ mol^{-1}) indicate that early, lower-barrier pathways dominate conversion under the present conditions. This is consistent with a prominent hemicellulose contribution in the main devolatilization regime. When contrasted with DAEM studies on hardwoods, our E_0 lies below typical literature means for component-resolved fits. This difference can be attributed to (i) the single-distribution representation and (ii) the emphasis on the major mass-loss window.

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