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Editorial

Kinetic Modelling of Biomass Pyrolysis Processes

Carmen Branca [1,*] and Antonio Galgano [2]

[1] Istituto di Scienze e Tecnologie per l'Energia e la Mobilità Sostenibili (STEMS), C.N.R., P.le V. Tecchio, 80125 Napoli, Italy
[2] Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università degli Studi di Napoli "Federico II", P.le V. Tecchio, 80125 Napoli, Italy; agalgano@unina.it
* Correspondence: carmen.branca@stems.cnr.it; Tel.: +39-081-7682232

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Pyrolytic conversion is the only biomass exploitation route capable of providing solid and liquid biofuels, as well as platform biomolecules for sustainable energy sources and raw materials for bio-based products. All biomass components are thermally degradable, allowing for complete transformation under appropriate heating conditions. The distribution and quality/composition of products depend on the properties of the feedstock and the thermal conditions under which the conversion is carried out. To develop efficient plant design and select optimal operating conditions, advanced computational tools are necessary. This involves coupling reaction kinetics with the mathematical description of other relevant physical phenomena in pyrolysis reactors.

Kinetic analysis is typically performed using standard thermogravimetric (TG) systems. However, the reliability of both the experimental data and the modelling may raise significant concerns. From the former aspect, initial sample mass/thickness, particle size, and heating rate must be accurately determined to guarantee negligible inclusion of transport phenomena and strict control of the reacting sample temperature [1–6]. These aspects are particularly relevant for certain agricultural residues which demonstrate an exothermic behaviour in pyrolysis that can ultimately lead to a pyrolytic runaway [7]. The analysis is further complicated by the significant variability in biomass, even within the same class, with different contents and nature of the biomass macro-components, as well as by the catalytic action of the inorganics [8]. Another major complication lies in separating the effects of the simultaneous occurrence of primary and secondary pyrolysis reactions. Establishing kinetic control in primary weight loss measurements is difficult owing to these factors. The mathematical and modelling aspects are also complex due to the variety of possible approaches, including model fitting (single-stage pyrolysis mechanisms and multi-component devolatilization mechanisms) and model-free (iso-conversion) methods, as well as distributed activation energy models (DAEM). Consequently, even in the case of biomass macro-components and standard feedstocks (e.g., wood), large variations in estimated activation energies are often reported.

From the points outlined above, research efforts should be directed towards determining the intrinsic kinetics of general validity, accounting for the effects of peculiar chemical composition, presence of catalysts, and pre-treatments. Another crucial aspect of kinetic analysis is the interpretability of model parameters from a chemical–physical point of view. The necessary connection between mathematical formulations and the thermal degradation of biomass components should always be considered. This may be achieved by the introduction of pseudo-components, i.e., the "kinetic components" of biomass, accounting for the strong overlap in the degradation of chemical components.

In this Special Issue of *Processes*, nine original research papers were accepted for publication and included, as listed in order of publication, at the end of this brief editorial and in Table 1. The covered topics concern (a) the devolatilization behaviour and kinetics of agro-industrial by-products and wastes, (b) the effects of feedstock torrefaction on successive conversion processes, and (c) the influence of catalysts on conversion dynamics and product distribution. In relation to the feedstock, three papers examined residues or wastes obtained as by-products from industrial plants, namely empty fruit bunches (8), DDGS (5), and peach stones (3), with the aim of improving the energy and material efficiency of biorefineries; two papers considered wastes such as RDF (6) and livestock manure (7), with the aim of reducing the environmental and economic impact of their disposal. Finally, two papers examined biomass macro-components (lignin (4) and cellulose (2)), and one torrefied wood (9). Of great practical interest are the results concerning the biomass with peculiar chemical composition such as solid by-products from the palm oil (8) and bioethanol (5) industries, since their thermal degradation characteristics are highly different from those observed for standard lignocellulosic biomass, both qualitatively and quantitatively. Given the presence of non-structural components, conversion takes place over a much wider temperature range at slower rates. Consequently, the activation energies can be lower than those typically estimated for lignocellulosic fuel. For the same reason, the results on the pyrolytic behaviour of non-conventional lignocellulosic biomasses (3) are relevant.

Noteworthy are also the results concerning the effects of torrefaction pretreatment (1, 9), proven to modify the reactivity of both biomass (1) and the produced char (9). Thermal pre-treatment has been shown to be effective in increasing the stability of the biochemical conversion of breeding sludge (7), providing potentially useful guidance for the management of the excessive quantities of such waste. In the same line of handling/recycling of wastes is the application of pyrolysis as a possible route for producing hydrogen-rich gas from municipal solid waste (6). Finally, studies on the thermal degradation of macro-components (4, 2) continue to be of major scientific importance. Indeed, though the degradation characteristics (temperatures, dynamics, products) have been established, much remains to be understood about their interactions during pyrolysis and the behaviour of the native components.

Regarding the modelling approach, three studies (3, 5, 9) employed model fitting methods, based on multi-component devolatilization mechanisms, while one (8) applied both a model free iso-conversional method and a distributed activation energy model. In two papers (2, 4), models based on a time derivative-generalized logistic function, used for crystallization phenomena, have been proposed to simulate the measured TG curves and evaluate the kinetic parameters. Finally, three studies (1, 6, 7) provided experimental results, with advice potentially useful for future kinetic analyses, although they did not include kinetics evaluations.

A brief overview of the contents of the nine papers is given below.

(1) Goldšteins et al. (2021)—The applicability of microwave torrefaction to achieve optimal biomass fuel combustion was investigated. This pretreatment leads to an increase in the porosity and reactivity of commercial straw, wood, and peat pellets, so improving their combustion performance in terms of both heat production and combustion product composition is of significance.
(2) López-Beceiro et al. (2021)—An estimation of the thermal degradation rate of cellulose at different temperatures was provided based on isothermal TG measurements mathematically described with a crystallization-type kinetic model based on time derivative logistic functions.
(3) Altantzis et al. (2021)—The pyrolysis kinetics of oil-extracted peach seeds, a fruit processing agro-industrial solid waste, was evaluated based on plug flow bench-scale reactor experiments. The effect of pyrolysis temperature, heating rates, and nitrogen flow was investigated. The fuel quality index showed the suitability of this biomass as feedstock for thermochemical conversion.
(4) López-Beceiro et al. (2021)—The complexity of the thermal degradation behaviour of lignin was confirmed in this study, highlighting the multistage nature of the process requiring specific thermogravimetric measurements, preferably including step-wise temperature programs, for kinetic analysis.
(5) Branca and Di Blasi (2021)—This study dealt with the thermal devolatilization behaviour and kinetics of DDGS, the major by-product of the bioethanol industry.

Given the peculiar chemical composition rich in protein, starch, and other minor non-structural components, the devolatilization occurs over a much wider temperature range and at slower rates than wood, corresponding to lower activation energies.

(6) Kusz et al. (2022)—This paper addresses the utilization of biochar produced from the pyrolysis of refuse-derived fuel (RDF) as a catalytic bed for promoting the cracking at high temperatures of the primary condensable vapours from the thermal degradation of the same RDF during the first stage of the process. The aim was to obtain a simple, low-cost method to produce pyrolytic gas with a high hydrogen content.

(7) Vanegas et al. (2022)—This study demonstrated that a mild thermal pre-treatment of livestock manure to be converted via anaerobic digestion significantly reduced the biomass acidification and oxygen demand, and globally improved the stability of biogas production.

(8) Suárez Useche et al. (2022)—The catalytic effect of zinc sulphate on the pyrolysis of empty fruit bunches, the largest fraction of solid residue from the oil palm industry, was evaluated via TG-FTIR analysis. For the conditions under examination, the conversion dynamics and kinetics and the product distribution were only slightly affected by the catalyst.

(9) Branca and Di Blasi (2023)—The effect of the torrefaction conditions (temperature and holding time) on char oxidation behaviour and kinetics were investigated via thermogravimetric analysis. As the torrefaction severity increased, the oxidation rates became slower and the two stages were well-described by a linear and a power–law rate reaction, respectively. Torrefaction caused lower activation energies with respect to untreated wood.

Table 1. Papers published in the Special Issue "Kinetic Modelling of Biomass Pyrolysis Processes".

N.	First Author and Corresponding Author	Corresponding Author's Institution	Title and Topic	DOI
1	Goldšteins, Zake	Institute of Physics, University of Latvia, Salaspils (Latvia)	Thermal Decomposition and Combustion of Microwave Pre-Treated Biomass Pellets (topic b)	https://doi.org/10.3390/pr9030492
2	López-Beceiro, Artiaga	Escola Politécnica Superior, University of A Coruña, Ferrol (Spain)	A Logistic Approach for Kinetics of Isothermal Pyrolysis of Cellulose (topic a)	https://doi.org/10.3390/pr9030551
3	Altantzis, Zabaniotou	Department of Chemical Engineering, Aristotle University of Thessaloniki, (Greece)	Apparent Pyrolysis Kinetics and Index-Based Assessment of Pretreated Peach Seeds (topic a)	https://doi.org/10.3390/pr9060905
4	López-Beceiro, Artiaga	Escola Politécnica Superior, University of A Coruña, Ferrol (Spain)	The Complexity of Lignin Thermal Degradation in the Isothermal Context (topic a)	https://doi.org/10.3390/pr9071154
5	Branca	Institute of Sciences and Technologies for Sustainable Energy and Mobility-CNR, Napoli (Italy)	Thermal Devolatilization Kinetics of Dry Distiller's Grains with Solubles (topic a)	https://doi.org/10.3390/pr9111907
6	Kusz, Kardas	Institute of Fluid Flow Machinery, Polish Academy of Sciences, Gdansk (Poland)	Pyrolysis of RDF and Catalytic Decomposition of the Produced Tar in a Char Bed Secondary Reactor as an Efficient Source of Syngas (topic c)	https://doi.org/10.3390/pr10010090

Table 1. *Cont.*

N.	First Author and Corresponding Author	Corresponding Author's Institution	Title and Topic	DOI
7	Vanegas	Research Group KAÍ, Universidad del Atlántico (Colombia)	Pilot-Scale Anaerobic Digestion of Pig Manure with Thermal Pretreatment: Stability Monitoring to Improve the Potential for Obtaining Methane (topic b)	https://doi.org/10.3390/pr10081602
8	Suárez Useche [1], Castillo Santiago [2]	[1] Bioprocess Faculty of Engineering, Universidad del Atlántico (Colombia) [2] LATERMO, Fluminense Federal University (Brazil)	Evaluation of the Zinc Sulfate Catalytic Effect in Empty Fruit Bunches Pyrolysis (topic c)	https://doi.org/10.3390/pr10091748
9	Branca	Institute of Sciences and Technologies for Sustainable Energy and Mobility-CNR, Napoli (Italy)	Oxidative Conversion of Chars Generated from the Fixed-Bed Pyrolysis of Wood Torrefied at Different Temperatures and Holding Times (topic b)	https://doi.org/10.3390/pr11040997

Conflicts of Interest: The authors declare no conflict of interest.

List of Contributions

1. Goldšteins, L.; Valdmanis, R.; Zak, M.; Arshanitsa, A.; Andersone, A. Thermal Decomposition and Combustion of Microwave Pre-Treated Biomass Pellets. *Processes* **2021**, *9*, 492.
2. López-Beceiro, J.; Díaz-Díaz, A.M.; Álvarez-García, A.; Tarrío-Saavedra, J.; Naya, S.; Artiaga, R. A Logistic Approach for Kinetics of Isothermal Pyrolysis of Cellulose. *Processes* **2021**, *9*, 551.
3. Altantzis, A.; Kallistridis N.; Stavropoulos, G.; Zabaniotou, A. Apparent Pyrolysis Kinetics and Index-Based Assessment of Pretreated Peach Seeds. *Processes* **2021**, *9*, 905.
4. López-Beceiro, J.; Díaz-Díaz, A.M.; Álvarez-García, A.; Tarrío-Saavedra, J.; Naya, S.; Artiaga, R. The Complexity of Lignin Thermal Degradation in the Isothermal Context. *Processes* **2021**, *9*, 1154.
5. Branca, C.; Di Blasi, C. Thermal Devolatilization Kinetics of Dry Distiller's Grains with Solubles (DDGS). *Processes* **2021**, *9*, 1907.
6. Kusz, B.; Kardas, D.; Heda, L.; Trawinski, B. Pyrolysis of RDF and Catalytic Decomposition of the Produced Tar in a Char Bed Secondary Reactor as an Efficient Source of Syngas. *Processes* **2022**, *10*, 90.
7. Vanegas, M.; Romani, F.; Jiménez, M. Pilot-Scale Anaerobic Digestion of Pig Manure with Thermal Pretreatment: Stability Monitoring to Improve the Potential for Obtaining Methane. *Processes* **2022**, *10*, 160.
8. Suárez Useche, A.M.; Santiago, Y.C.; Restrepo, J.B.; Albis Arrieta, A.R.; Agámez Salgado, K.P. Evaluation of the Zinc Sulfate Catalytic Effect in Empty Fruit Bunches Pyrolysis. *Processes* **2022**, *10*, 1748.
9. Branca, C.; Di Blasi, C. Oxidative Conversion of Chars Generated from the Fixed-Bed Pyrolysis of Wood Torrefied at Different Temperatures and Holding Times. *Processes* **2023**, *11*, 997.

References

1. Anca-Couce, A. Reaction mechanisms and multi-scale modelling of lignocellulosic biomass pyrolysis. *Prog. Energy Combust. Sci.* **2016**, *53*, 41. [CrossRef]
2. Wang, S.; Dai, G.; Yang, H.; Luo, Z. Lignocellulosic biomass pyrolysis mechanism: A state-of-the-art review. *Prog. Energy Combust. Sci.* **2017**, *62*, 33. [CrossRef]

3. Ciesielski, P.N.; Pecha, M.B.; Lattanzi, A.M.; Bharadwaj, V.S.; Crowley, M.F.; Bu, L.; Vermaas, J.V.; Steirer, K.X.; Crowley, M.F. Advances in multiscale modeling of lignocellulosic biomass. *ACS Sustain. Chem. Eng.* **2020**, *8*, 3512. [CrossRef]
4. Kaczor, Z.; Bulinski, Z.; Sebastian Werle, S. Modelling approaches to waste biomass pyrolysis: A review. *Renew. Energy* **2020**, *159*, 427. [CrossRef]
5. Vikram, S.; Rosha, P.; Kumar, S. Recent modeling approaches to biomass pyrolysis: A review. *Energy Fuels* **2021**, *35*, 7406. [CrossRef]
6. Attanayake, D.D.; Sewerin, F.; Kulkarni, S.; Dernbecher, A.; Dieguez-Alonso, A.; van Wachem, B. Review of modelling of pyrolysis processes with CFD-DEM. *Flow Turbul. Combust.* **2023**, *111*, 355. [CrossRef]
7. Branca, C.; Galgano, A.; Di Blasi, C. Dynamics and products of potato crop residue conversion under a pyrolytic runaway regime—Influences of feedstock variability. *Energy* **2023**, *256*, 127507. [CrossRef]
8. Di Blasi, C.; Branca, C.; Sarnataro, F.E.; Gallo, A. Thermal Runaway in the Pyrolysis of Some Lignocellulosic Biomasses. *Energy Fuels* **2014**, *28*, 2684. [CrossRef]