

Modification of Biomass Combustion Kinetics by Additives and Torrefaction: A Study on Meadow Hay

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Abstract

This study investigates the combustion kinetics of raw and torrefied meadow hay and hay-based mixtures containing organic and inorganic additives. Thermogravimetric analysis was performed under an oxidizing atmosphere at different heating rates, and kinetic parameters were determined using the integral isoconversional OFW and KAS methods. Both methods showed very good agreement, KAS was selected for subsequent analysis. The results confirmed the multi-stage nature of biomass combustion, involving overlapping reactions associated with hemicellulose, cellulose, lignin, and char oxidation.

1. Introduction

The use and further development of renewable energy sources is important to achieve carbon neutrality. Waste and surplus biomass from agriculture and forestry represents a significant source of bioenergy [1]. Bioenergy contributed 56 EJ, approximately 9% of global energy supply, the highest level to date and a 2% increase in value compared to 2022. Solid biomass (pellets, briquettes and traditional uses) accounted for more than 83% of supply [2]. Biomass energy is the chemical energy produced by the conversion of solar energy during photosynthesis [3]. This energy is considered carbon neutral under sustainable conditions [4].

A common method of agricultural waste treatment is the conversion of biomass into energy through physical, biological, or thermochemical processes [5]. Thermochemical conversion relies on heat to decompose biomass into energy-rich products, with the main pathways being combustion, gasification and pyrolysis [6]. Pyrolysis is carried out at moderate temperatures (approximately 350–700°C) in the absence or near absence of oxygen, producing solid, liquid, and gaseous fuels [7]. From a co-combustion perspective, biomass is advantageous due to its high volatile matter content, relatively low ash content, and good reactivity during combustion [8]. Various materials can be co-combusted, from traditional types of biomass to waste, such as sewage sludge and toners powder [9]. However, the thermochemical processing of biomass is often challenging due to its heterogeneous composition, low energy density, and high moisture content [10].

To address these limitations, various pretreatment methods, including pelletization, briquetting, and torrefaction, are commonly applied [11].

As a result, torrefied biomass exhibits improved properties, including higher energy density, lower moisture content, enhanced grindability, and increased carbon-to-hydrogen and carbon-to-oxygen ratios [12].

This article addresses the impact of torrefaction on biomass combustion. Torrefaction is a thermal process causing hemicellulose depolymerization, partial dehydration, and aromatization of the structure, and consequently, an increase in the fixed carbon content and a decrease in oxygen content [13].

Various binders can be added to biomass, which affect, for example, the thermochemical properties of fuels [14]. Binders are organic and inorganic, and there are more than fifty types of binders that can be used in biomass processing [15]. Organic binders include lignin, liginosulfonate, starch, flour, carboxymethylcellulose, molasses, glycerol, and others. Inorganic binders include magnesium and calcium carbonate, calcium oxide, sodium hydroxide, etc. [16, 17].

The presence of organic and inorganic additives in raw biomass also causes certain changes in the pyrolysis and combustion processes [18, 19]. Synergistic effects between additives and torrefaction on the thermal treatment of biomass can also be expected [20].

This research focuses on evaluating the individual and combined effects of torrefaction and selected organic and inorganic additives on the combustion behavior of meadow hay.

2. Materials and Methods

2.1. Material

Samples of pure meadow hay (H) and hay with additives, after pelletization, were used in the study. From the mixtures presented in Sykorova et al. [21], the following samples were selected: 100H, 2S, 2CMC and 2MC (Table 1). The biomass samples were prepared as pellets with a diameter of 6 mm. The content of individual additives, both organic (starch and carboxymethylcellulose) and inorganic (magnesium carbonate), was fixed at 2%, as higher amounts would result in a dominant ash effect in the analysis, making interpretation more difficult.

Table 1
Samples used in the investigation.

Composition	Sample symbol	
	Raw	After torrefaction
100% hay	100H	100H TORR
2% wheat starch + 98% hay	2S	2S TORR
2% carboxymethylcellulose + 98% hay	2CMC	2CMC TORR
2% magnesium carbonate + 98% hay	2MC	2MC TORR

2.2. Torrefaction

Torrefaction was carried out in a small laboratory batch reactor at a temperature of 250°C in a nitrogen atmosphere, with a residence time of 2 hours.

2.3. Thermal analysis

The meadow hay samples were subjected to thermogravimetric analysis using a NETZSCH analyzer, model STA 449 F3 Jupiter.

The experimental data recorded within the temperature range of 50–1000°C was used to calculate the kinetic parameters, i.e., activation energy (E_a), and the Arrhenius constant (A).

2.4. Kinetic parameters calculations

NETZSCH Kinetics Neo® software was used to calculate kinetic parameters. In case of raw meadow hay sample (100H) two model-free, isoconversion methods were employed: (1) Kissinger-Akahira-Sunose (KAS); and (2) Ozawa-Flynn-Wall (OFW).

Kinetic parameters of combustion process can be derived using various approaches, including both model-based and model-free techniques.

The applied isoconversional methods are based on the assumption that the reaction mechanism remains unchanged within a given temperature range and that the activation energy is constant for a specific degree of conversion (α), although it may vary during the course of the reaction. These methods are model-free, meaning that the reaction rate at a constant degree of conversion is assumed to depend solely on temperature. Consequently, the activation energy can be evaluated without specifying a particular reaction model [22]. Both methods employed in this study are widely used for modelling the kinetics of biomass decomposition, including both pyrolysis and combustion processes [23, 24].

2.4.1 Kissinger-Akahira-Sunose method

The KAS kinetic method is an integral isoconversional method, where the activation energy is a function of the conversion degree of a chemical reaction, and can be applied without any assumption concerning the kinetic model [25].

2.4.2 Ozawa-Flynn-Wall method

Ozawa, Flynn and Wall developed a model-free method, where the measurements are analysed for multiple conversion levels. Activation energy is determined without assumption of reaction type by using of points with the same conversion from the measurements with different heating rates or different isothermal conditions.

The KAS method was selected to test the remaining samples, based on which the average values of activation energy and pre-exponential factor A of the combustion process were calculated.

2.5. Microstructural characterization

A Keyence VHX digital microscope (Keyence, Japan) was used to characterize the materials. This involved characterizing the homogeneity of the material in terms of the "coating" of individual hay fibers with added additives.

3. Results and discussion

3.1. Combustion process

The decomposition of the hay sample (100H) in the oxidizing atmosphere proceeded in multiple stages. In the temperature range of 30–150°C, the sample dehydrated, resulting in a 6.35% mass loss. The main combustion process begins at approximately 150°C and proceeds in two stages.

3.2. Kinetics of combustion

The thermogravimetric studies conducted allowed the determination of kinetic parameters for the combustion of hay samples.

3.2.1 Kissinger-Akahira-Sunose (KAS) method

As a result of the analysis, the values of activation energy (E_a), and the Arrhenius constant (A) for individual conversion degrees (α) were obtained (Fig. 1b and 1c). Figure 1a presents the dependence of the $\log(\beta/T^2)$ value on the inverse of temperature ($1/T$) for points with the same conversion.

3.2.2 Ozawa-Flynn-Wall (OFW) method

The Ozawa–Flynn–Wall (OFW) method was applied to determine the activation energy (E_a) at different conversion degrees (α), using thermogravimetric data obtained at different heating rates. For each conversion degree, the logarithm of the heating rate ($\ln \beta$) was plotted against the reciprocal absolute temperature ($1/T$) corresponding to the same conversion degree at each heating rate (Fig. 2a). The activation energy values obtained for conversion degrees ranging from 0.05 to 0.95 are presented in Fig. 2b.

3.3. Comparison of methods KAS and OFW

The kinetic parameters of the hay combustion reaction obtained using the KAS and OFW methods are very similar, and the coefficient of determination R^2 is 1. This confirms the correctness of the calculations and indicates the stability of the isoconversion analysis.

To assess the mechanism of the hay combustion process, a master plot was used, which compared the normalized course of the reaction function determined experimentally with theoretical kinetic functions corresponding to idealized reaction models.

Comparison of master plots derived from the OFW and KAS methods demonstrates good qualitative agreement, with the KAS-based plot demonstrating greater clarity in distinguishing theoretical kinetic models. This is due to the more accurate approximation of the temperature integral used in the KAS method, which translates into greater stability of the normalized reaction function, particularly in the range of medium and high conversion rates.

1. The influence of organic and mineral additives and torrefaction on the kinetics of the combustion process

Based on the results presented above, the KAS method was selected for further experiments. According to the methodology presented above, kinetic parameters were determined for biomass samples before and after the torrefaction process (Table 2).

Table 2
The values of the averaged E_a and the pre-exponential Arrhenius coefficient (A) for the samples combustion process, calculated by the KAS method.

Sample		E_a (kJ/mol)	Log A (Log(1/s))	R2
Raw	100H	132.33	9.28	1.0000
	2S	109.39	7.05	0.9836
	2CMC	123.86	8.37	0.9692
	2MC	138.99	9.71	0.9899

As can be seen from the presented results, a 2% addition of organic components (starch and carboxymethylcellulose) to raw samples reduces the activation energy. These additives catalyse oxidation processes, therefore lowering the energy barrier of the reaction. In contrast, the addition of magnesium carbonate results in higher apparent activation energy values, suggesting a less favorable combustion process under the investigated conditions.

3.5. Microstructural characterization of biomass–additive mixtures

Figure 6 shows the microstructural characterization of the coverage of meadow hay stalks by individual additives: starch (Fig. 3a), carboxymethylcellulose (Fig. 3b) and magnesium carbonate (Fig. 3c). Each additive has three pictures because each picture comes from a different location in the sample under the microscope to show that the distribution is homogeneous.

Digital microscopy confirmed that all additives used adhered to the surface of hay particles, with different patterns of distribution. Starch formed predominantly dispersed particles on the surface of the fibers (Fig. 6a), while carboxymethylcellulose formed a more continuous coating connecting individual straws (Fig. 6b). Magnesium carbonate was present in the form of fine mineral particles that locally covered the surface of the biomass and created an inorganic barrier between the hay and the surrounding environment (Fig. 6c).

4. Conclusions

The present study provides a comprehensive analysis of the combustion kinetics of meadow hay and hay-based mixtures containing selected organic and inorganic additives, both in raw and torrefied forms. Based on the obtained results, the following conclusions can be drawn:

- As a result of the cross-validation of the KAS and OFW methods, very high agreement was found between the obtained kinetic parameters. Due to the variation in biomass combustion kinetics parameters at different conversion levels, the use of isoconversion methods is justified.
- Biomass combustion is a complex, multistage process, involving overlapping reactions related to the degradation of hemicellulose, cellulose, lignin, and the subsequent oxidation of char. The variation of activation energy with the degree of conversion confirms that the mechanism changes during the reaction.
- The addition of organic additives (starch and carboxymethylcellulose) leads to a decrease in the apparent activation energy in raw samples, indicating changes in their combustion kinetics.
- In contrast, the inorganic additive (magnesium carbonate) increases the activation energy, which can be attributed to its inert character, dilution of the reactive biomass fraction, and the formation of mineral residues that introduce diffusion limitations and hinder oxygen access.

Abbreviations

A	Arrhenius constant, pre-exponential factor
α	Degree of conversion
CMC	Carboxymethylcelullose
DSC	Differential scanning calorimetry
DTG	Differential thermogravimetric
E_a	Activation energy
H	Hay
k	Reaction rate constant
KAS	Kissinger-Akahira-Sunose model
MC	Magnesium carbonate
OFW	Ozawa-Flynn-Wall model
R	Universal gas constant
S	Starch

Declarations

Conflicts of Interest:

The authors declare no conflict of interest.

Declaration of generative AI

During the preparation of this work the authors used ChatGPT Pro in order to stylistic refinement and improved readability. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

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Data Availability Statement:

The data presented in this study are available at <https://zenodo.org/records/23032900>.

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Figures

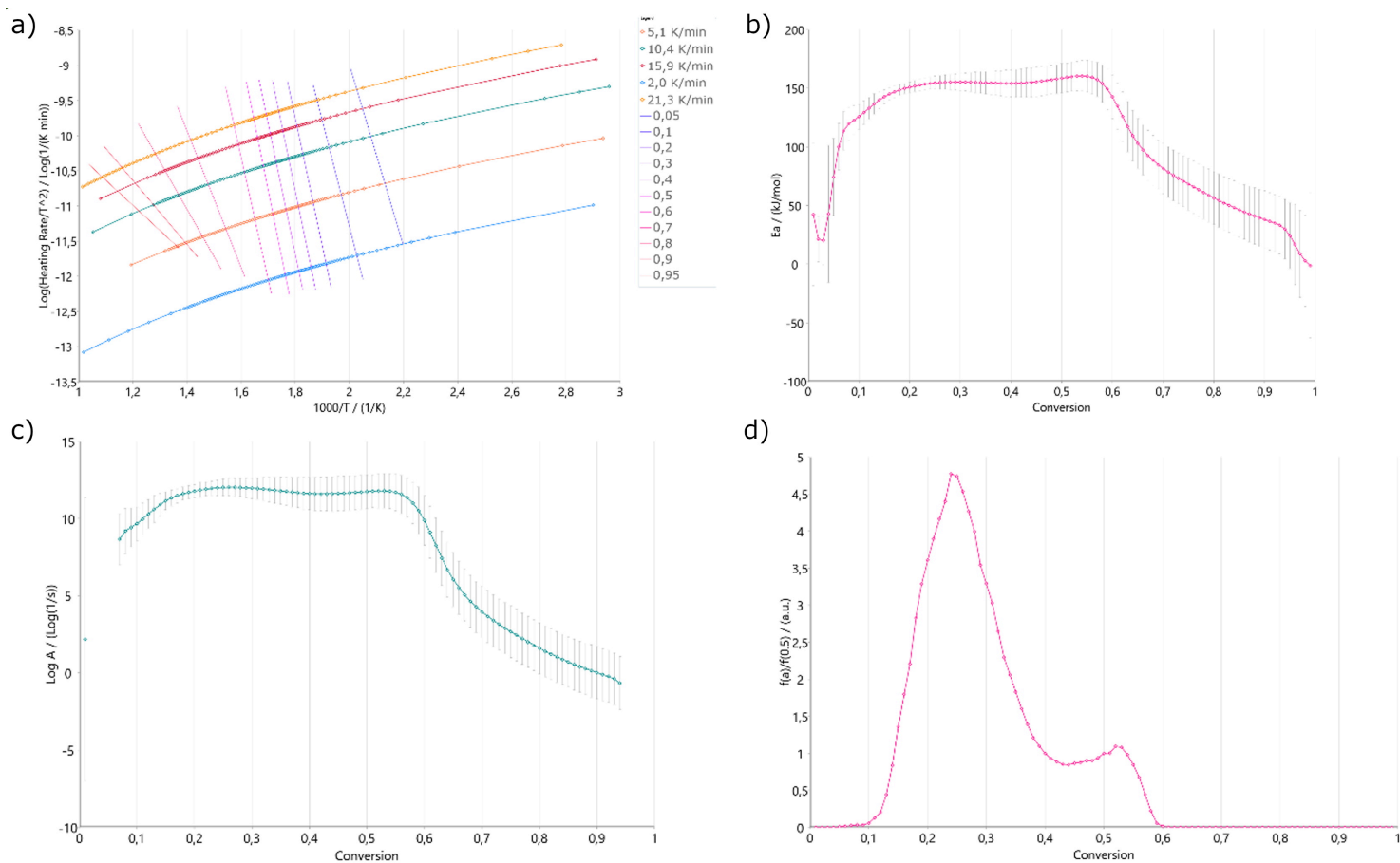


Figure 1

KAS kinetic analysis for a hay sample (H100). Linear fit curves for conversion from (a), dependence of the activation energy E_a on the degree of conversion α (b), dependence of the Arrhenius constant A on the degree of conversion α (c), master plot (d).

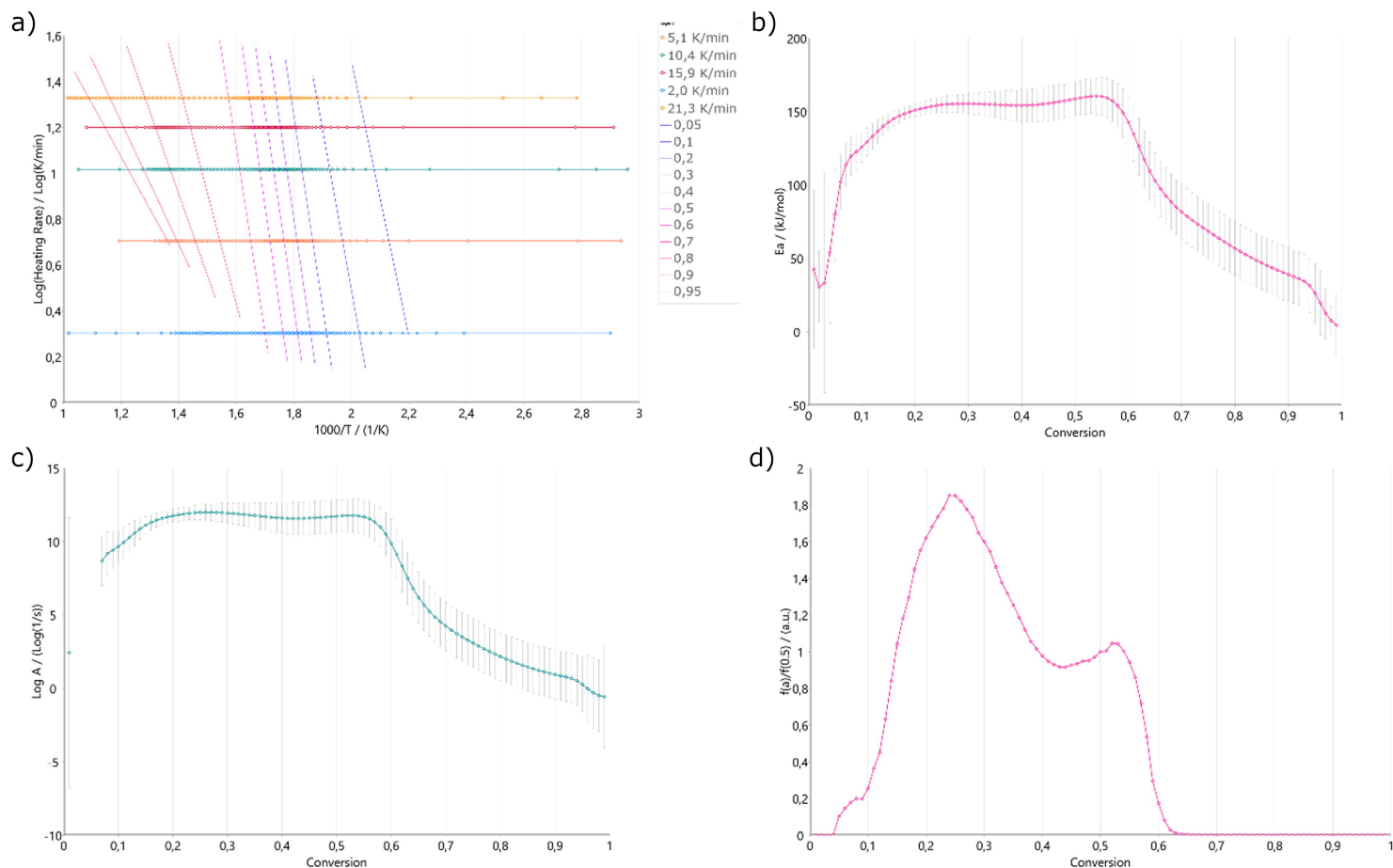


Figure 2

OFW kinetic analysis for a hay sample (H100). Linear fit curves for conversion (a), dependence of the activation energy E_a on the degree of conversion α (b), dependence of the Arrhenius constant A on the degree of conversion α (c), master plot (d).



Figure 3

Microscopic images of hay stalks coverage by individual additives