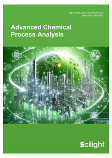
Scilight

Advanced Chemical Process Analysis
https://www.sciltp.com/journals/acpa



Article

Modeling and Optimization of Thermal Stability and Heat Release Capacity of Waste Mixtures with Biomass Residues (*Chlorella vulgaris*)

Loredana-Vasilica Postolache *, Gabriela Soreanu, Igor Cretescu and Gabriela Lisa

"Cristofor Simionescu" Faculty of Chemical Engineering and Environmental Protection, "Gheorghe Asachi" Technical University of Iasi, 73 Prof. D. Mangeron Blvd., 700050 Iasi, Romania
* Correspondence: loredana-vasilica.postolache@student.tuiasi.ro

How To Cite: Postolache, L.-V.; Soreanu, G.; Cretescu, I.; et al. Modeling and Optimization of Thermal Stability and Heat Release Capacity of Waste Mixtures with Biomass Residues (*Chlorella vulgaris*). *Advanced Chemical Process Analysis* **2025**, *1*(1), 6. https://doi.org/10.53941/acpa.2025.100006

Received: 2 October 2025
Revised: 12 December 2025
Accepted: 15 December 2025
Published: 18 December 2025

Abstract: This paper investigates the thermal behavior of binary mixtures composed of spent biomass of Chlorella vulgaris (CHo) and various types of waste, using thermogravimetric analysis (TGA) and micro-combustion calorimetry (MCC) in both oxidizing (air) and inert (nitrogen) atmospheres. The results showed that the nature of the waste and the type of atmosphere strongly influence the degradation processes. In air, mixtures with lignocellulosic (CHo-G) and textile (CHo-T) components favored complete oxidation, characterized by early ignition, low residue, and moderate thermal stability. In nitrogen, the CHo-A and CHo-P mixtures exhibited efficient pyrolysis, with lower decomposition temperatures (Ts) and reduced amounts of residue. From an energy perspective, CHo-P mixtures exhibited the highest calorific parameters (HRC and THR), which makes them suitable for direct energy recovery applications. Influence score analysis confirmed the superior performance of CHo-G mixtures (3.35–3.56), due to synergistic interactions between algal biomass and woody compounds. In contrast, CHo-C mixtures exhibited low energy efficiency and modest thermal behavior. The conclusions emphasize that the selection of waste type and working atmosphere is essential for optimizing thermochemical conversion, highlighting the potential of CHo mixtures for sustainable energy recovery applications.

Keywords: *Chlorella vulgaris*; solid waste; modeling; synergistic effect; TGA; MCC

1. Introduction

Modeling and optimizing the thermal stability and heat release capacity of waste mixtures with biomass residues has been the main focus of numerous studies. The integration of advanced kinetic and thermodynamic methods provides an in-depth understanding of co-processing processes through co-pyrolysis, facilitating the development of efficient technologies for recycling and thermal recovery of waste and biomass [1,2]. Modeling heat release capacity and total heat flux also helps in selecting the best waste mixture to maximize its potential for co-processing in cement plants. Numerous researchers have used a variety of modeling techniques to optimize this process. Numerical modeling, modeling with chemical industry software, and the use of various AI tools are some of these methods [3–6]. Modeling of higher heating value (HHV) based on the elemental composition of biomass solid waste (BSW) was performed using empirical correlations derived by multiple regression. This process had high accuracy ($R^2 > 0.9$) and a prediction error of less than 15%. This method helps to estimate the energy performance of different combinations of BSW and assists in choosing the best method of energy recovery [3]. The activation energy, pre-exponential factor, and thermodynamic parameters were determined in addition to the pyrolysis analysis of Nanche BSC stone (*Byrsonima crassifolia*) using kinetic models obtained from nonisothermal thermogravimetric experiments. These findings allowed the modeling of the pyrolytic degradation process and demonstrated that this residue is capable of generating bioenergy [5].

Conclusive results regarding the reduction of the energy barrier in plastic waste degradation and the fact that predictive modeling based on artificial intelligence could be useful for optimizing pyrolysis were obtained in a recent study by Gandhi et al. [7]. Another recent study evaluated how plastic composition influences interactions, kinetics, and product yields in the co-pyrolysis of date palm waste (DPW) and polyethylene foam (PEF) mixtures [8]. Co-pyrolysis tests in a fixed-bed reactor, as part of the study by Nawaz and Razzak [8], showed that the maximum bio-oil yield (38.85%) was obtained at an equal ratio of 50% PEF and 50% DPW. Consequently, combining PEF and date palm waste is a promising option for improving the recovery process through pyrolysis [8].

The co-pyrolysis of polyethylene terephthalate (PET) and Samanea saman seeds (SS) was examined to determine the reaction kinetics and synergistic effects of these two raw materials [9]. To determine the kinetic parameters, several isoconversional models were used to study mixtures of SS and PET in different proportions, with the results showing that the 3:1 SS/PET mixture produced the highest yield of volatile compounds and the strongest synergistic effect at high temperatures [9]. Another study investigates the co-pyrolysis of tea stems (TS) with PET, focusing on the interactions between them during pyrolysis [10]. The results show that the TS/PET ratio is the main factor determining synergy. The mixture with 25% TS and 75% PET showed the least antagonistic effects, while the one with 75% TS and 25% PET showed both positive and negative synergistic effects. There is the presence of oxygenated compounds, which indicates the formation of aromatic hydrocarbons in the co-pyrolysis process, according to FT-IR spectroscopy [10].

Thermogravimetry, complex pyrolysis (Py) technique, gas chromatography (GC), and mass spectrometry (MS) were used to investigate the co-pyrolysis of *Chlorella pyrenoidosa* algae with polystyrene (PS). Distinct stages of decomposition and a significant synergistic impact were found at a ratio of 1:1. There was a decrease in apparent activation energy and favorable changes in the composition of the bio-oil, characterized by an increase in aromatic hydrocarbons and a decrease in oxygenated and nitrogenated compounds. This method offers a viable solution for the sustainable recovery of plastic and biomass waste [11].

In this paper, mixtures of waste with spent biomass from Chlorella vulgaris, originating from a photobioreactor designed for carbon dioxide capture, were investigated using numerical modeling and optimization methods. There are several studies that have examined co-pyrolysis and numerical modeling of biomass mixtures with different types of waste, but few studies have examined the use of residual biomass from Chlorella vulgaris photobioreactors for carbon dioxide capture as co-incineration material in cement plants. The novelty of this study consists in the use of residual biomass from Chlorella vulgaris photobioreactors integrated with TGA and MCC experimental data to develop a predictive model that optimizes the thermal stability and heat release capacity of the mixtures, with direct applications in co-processing and energy recovery in the cement industry. In addition, the use of residual biomass from CO_2 capture processes is in line with the principles of the circular economy, by reintegrating a secondary stream into a sustainable energy application, thus contributing to both emission reduction and efficient resource recovery.

2. Materials and Methods

The materials used for the study were a series of waste products, such as: plastic waste-P, textiles-T, cardboard-C, tires-A, used railroad ties-G, and microalgae residues-CHo. Plastic waste consists mainly of polyethylene terephthalate. The textile waste consists of a mixture of cotton and synthetic fibres. A tire intended for off-road use was used to obtain a sample of worn tire. The used railroad ties were procured from the regional branch of the railroad in Iași, while the microalgae residues came from a carbon dioxide capture photobioreactor.

The study evaluated the impact of using CHo biomass in binary mixtures with waste: C, G, T, P, and A on the thermal decomposition process. To create the mixtures, the mass fraction of CHo was considered as an independent variable in the planning of the experiments. This varied between 15 and 45% with a central value of 30% and a variation range of the independent variable of ±15%. Thermal analyses of the samples were conducted under dynamic conditions in both air and nitrogen environments, at a flow rate of 20 mL/min, a heating rate of 10 °C/min, across a temperature range of 25–700 °C, with sample masses of approximately 7 mg. Thermogravimetric measurements were performed using a Mettler Toledo TGA/SDTA 851^e, a high-precision instrument capable of TG, DTG, and DTA analyses with controlled temperature and heating rates. The system, operated through the STAR SW software for automated data acquisition and evaluation, was calibrated for DTA using certified standard metals (In, Al, and Au) following the manufacturer's specifications. All experiments were carried out in 40 µL alumina crucibles equipped with lids containing an evacuation hole, ensuring high thermal stability and reproducible measurement conditions. Based on the two thermogravimetric curves (TG and DTG), the amount of residue remaining after the process was obtained, as well as the values of the statistical heat resistance index (T_s), obtained using the equation:

$$T_S = 0.49 \times [T_{5\%}+0.6(T_{30\%} - T_{5\%})] \tag{1}$$

where $T_{5\%}$ is the temperature at which 5% of the sample mass was lost, and $T_{30\%}$ represents the temperature corresponding to the loss of 30% of the sample mass. In both cases, initial moisture losses were neglected, if any.

The binary mixtures were previously analyzed by thermogravimetric analysis in air and nitrogen, as well as by micro combustion calorimetry (MCC). MCC tests were performed under regulated conditions, featuring a gradual rise in temperature within the pyrolyzer at a heating rate of 1 °C/s from 25 °C to 750 °C, in a nitrogen environment with a flow rate of 80 cm^3/min. The gases produced by the pyrolysis process subsequently move into the combustor, where they ignite at a steady temperature of 900 °C, and the combustion continues for 600 seconds. The sample volatiles were fully oxidized in the combustor to determine the total heat release (THR), and the instrument was calibrated using standard procedures, including verification of gas flow and heat-release detection, ensuring accurate and reproducible measurements. The results obtained from the experiments were used to create the database that was used for statistical processing. Following the thermogravimetric analysis of the mixtures, a database was created that includes the percentage amounts of residue and the T_s values calculated for the two working environments. The database obtained by applying the MCC technique consists of the results obtained for the following parameters: the amount of residue following MCC analysis- Char Yiled, total heat released (THR), the time at which the first maximum heat release rate is recorded (TIME1), and heat release capacity (HRC).

The statistical processing of the available experimental data was performed using the specialized software SigmaPlot 11.00 (Systat Software Inc., San Jose, CA, USA). Using this method, information was obtained on the mean values, standard deviation, standard error of the mean, confidence interval of the mean, amplitude, maximum and minimum values, median, distribution intervals (25% and 75%) data, asymmetry and kurtosis tests, Kolmogorov-Smirnov test, Shapiro-Wilk test for assessing the normality of data distribution. The sum of values and the sum of squares were also calculated, the latter being a measure of deviation from the mean value [12]. To check for statistically significant differences between pairs of data series, the Kruskal-Wallis test was applied, including the multiple comparison procedure for pairs (Student–Newman–Keuls method). The test statistic for one-way analysis of variance is calculated as the ratio of the sum of squares of the experimental data sets to the sum of squares of the residuals. The Kruskal-Wallis test belongs to the category of nonparametric tests and is based not on raw values but on data ranks [13]. When the Kruskal-Wallis test indicates a significant result, it can be concluded that at least one of the groups differs significantly from the others. However, the test does not specifically indicate where these differences occur or how many there actually are [13].

3. Results and Discussion

Following thermogravimetric analysis and micro-scale combustion calorimetry, the following values were obtained for the parameters considered relevant for assessing the influence of adding CHo in mixture with different wastes, presented in Tables 1 and 2 [14].

Table 1. Amount of residue, statistical heat resistance index temperature (T_S) resulting from thermogravimetric analysis of CHo and waste mixtures.

CHo Concentration			0.0	0.2	0.3	0.5	1.0
Waste Type	**Working Atmosphere**	**Parameter**					
C	Air	Residue, %	16.7	20.6	21.1	18.7	13.1
		Ts, °C	149.0	139.0	136.0	126.0	143.0
	Nitrogen	Residue, %	30.5	36.6	35.0	33.4	33.5
		Ts, °C	160.0	155.0	154.0	151.0	142.0
A	Air	Residue, %	12.1	23.3	12.8	16.5	13.1
		Ts, °C	188.0	183.0	179.0	161.0	143.0
	Nitrogen	Residue, %	39.6	34.6	38.7	36.5	33.5
		Ts, °C	188.0	185.0	176.0	172.0	142.0
G	Air	Residue, %	22.3	6.4	7.4	7.1	13.1
		Ts, °C	157.0	123.0	129.0	116.0	143.0
	Nitrogen	Residue, %	22.1	23.2	25.8	25.6	33.5
		Ts, °C	159.0	144.0	141.0	140.0	142.0

Table 1. *Cont.*

CHo Concentration			**0.0**	**0.2**	**0.3**	**0.5**	**1.0**
Waste Type	**Working Atmosphere**	**Parameter**					
T	Air	Residue, %	0.8	6.0	8.3	8.9	13.1
		Ts, °C	153.0	153.0	145.0	138.0	143.0
	Nitrogen	Residue, %	3.5	20.2	22.7	26.4	33.5
		Ts, °C	164.0	163.0	160.0	153.0	142.0
P	Air	Residue, %	1.3	5.9	7.8	8.5	13.1
		Ts, °C	199.0	193.0	182.0	172.0	143.0
	Nitrogen	Residue, %	18.2	17.8	23.5	25.1	33.5
		Ts, °C	205.0	208.0	190.0	176.0	142.0

Table 2. Amount of residue, total heat released (THR), heat release capacity (HRC), time when the first maximum heat release rate value is recorded (TIME1) following MCC analysis.

CHo Concentration		**0.0**	**0.2**	**0.3**	**0.5**	**1.0**
Waste Type	**Parameter**					
C	Char Yield, %	25.1	28.8	26.4	29.4	27.7
	THR, kJ/g	9.4	8.2	9.3	9.3	10.8
	HRC, J/g·K	129.3	134.5	144.4	110.7	104.2
	TIME1, s	190.5	223.5	128.5	184.0	109.0
A	Char Yield, %	35.1	35.1	34.6	33.5	27.7
	THR, kJ/g	25.0	21.3	21.5	17.1	10.8
	HRC, J/g·K	391.5	327.6	224.8	217.5	104.2
	TIME1, s	208.0	157.5	177.5	171.5	109.0
G	Char Yield, %	15.3	17.8	20.1	22.0	27.7
	THR, kJ/g	12.9	12.6	12.5	12.0	10.8
	HRC, J/g·K	171.2	157.2	138.7	117.6	104.2
	TIME1, s	240.5	196.0	202.0	211.0	109.0
T	Char Yield, %	10.5	13.4	2.3	19.3	27.7
	THR, kJ/g	12.9	13.7	12.5	12.5	10.8
	HRC, J/g·K	262.4	255.6	209.4	170.1	104.2
	TIME1, s	175.5	235.5	251.0	196.5	109.0
P	Char Yield, %	10.8	12.7	0.0	19.5	27.7
	THR, kJ/g	17.2	16.1	15.2	13.8	10.8
	HRC, J/g·K	454.3	346.2	274.0	204.1	104.2
	TIME1, s	97.0	237.0	96.5	150.0	109.0

Numerical and graphical methods, known as descriptive statistics, are used to organize, present, and analyze data [15,16]. In this study, statistical processing of the data obtained from thermogravimetric analysis and MCC techniques was performed for binary waste-biomass mixtures. Based on the results of the statistical description of the data (Table 3), similar values of standard deviation are observed for the quantities of residue obtained from thermogravimetric analysis (columns 1 and 2). The amplitude, i.e., the difference between the maximum and minimum values, which indicates the range of values over which the experimental data distribution extends, has values between 17.37 and 77.26. The median, the statistical parameter indicating the middle of the data series, has values close to the average values, which shows a uniform distribution of the experimental data. The analysis of the experimental data distribution reveals a positive asymmetry for the 4 columns analyzed. The flattening indices of the variation curve of the analyzed data (kurtosis) have low values, which indicates a good distribution of data, i.e., there is little data that has values very different from the mean.

Table 3. Statistical description of experimental data from thermogravimetric analysis for CHo mixtures.

Column	**Size**	**Missing**	**Mean**	**Std. Dev.**	**Std. Error**	**C.I of Mean**	**Range**
Col. 1	15	0	11.954	6.289	1.624	3.483	17.370
Col. 2	15	0	28.336	6.745	1.741	3.735	20.900
Col. 3	15	0	151.646	25.037	6.464	13.865	77.260
Col. 4	15	0	164.535	19.531	5.043	10.816	67.286

Table 3. *Cont.*

Column	Max	Min	Median	25%	75%	Skewness	Kurtosis
Col. 1	23.260	5.890	8.540	7.178	18.180	0.750	−1.183
Col. 2	38.680	17.780	25.840	23.268	34.873	0.175	−1.443
Col. 3	192.787	115.527	144.932	130.783	176.776	0.268	−1.354
Col. 4	207.604	140.318	160.310	151.493	176.190	0.733	−0.0222
Column	**K-S Dist.**	**K-S Prob.**	**SWilk W**	**SWilk Prob.**	**Sum**	**Sum of Squares**	
Col. 1	0.287	0.002	0.825	0.008	179.310	2697.269	
Col. 2	0.212	0.069	0.911	0.142	425.040	12,680.775	
Col. 3	0.167	0.304	0.933	0.307	2274.695	353,724.847	
Col. 4	0.149	0.453	0.939	0.365	2468.030	411,418.690	

Col. 1—residue quantity (%) in air, Col. 2—residue quantity in nitrogen (%), Col. 3—T_s values (°C) in air, Col. 4—T_s values in nitrogen (°C).

Following the Kruskal-Wallis test, the differences between the median values of the analyzed groups are greater than would be expected by chance, indicating a statistically significant difference (p = <0.001). This is evidenced by high values of the q parameter (Table 4) in the Student-Newman-Keul method.

Table 4. Results of the Kruskal-Wallis test of binary mixtures with CHo-thermogravimetric analysis.

Comparison	Diff. of Ranks	q	$p < 0.05$
Col 4 vs. Col 1	591.000	8.738	Da
Col 4 vs. Col 2	384.000	7.549	Da
Col 4 vs. Col 3	75.000	2.200	Nu
Col 3 vs. Col 1	516.000	10.144	Da
Col 3 vs. Col 2	309.000	9.063	Da
Col 2 vs. Col 1	207.000	6.071	Da

According to the q values from the Student-Newman-Keuls test presented in Table 4, it was established that there are no statistically significant differences (p > 0.05) between the Ts values for air (column 3) and the Ts values for nitrogen (column 4).

Table 5 presents the statistical description of the data obtained using the MCC technique. Low standard deviation values are observed in column 2, indicating a lower dispersion of these experimental data. The amplitude has values between 13.36 and 235.49. The uniform distribution of the experimental data is highlighted by the close values of the median to the mean values. A positive asymmetry is observed for columns 2 and 3, and a negative asymmetry for columns 1 and 4. The flattening indices of the variation curve of the analyzed data (kurtosis) have low values, which indicates a good distribution of the data.

Table 5. Statistical description of the experimental data from MCC for CHo mixtures.

Column	Size	Missing	Mean	Std. Dev.	Std. Error	C.I of Mean	Range
Col. 1	15	0	20.981	10.815	2.793	5.989	35.080
Col. 2	15	0	13.842	3.928	1.014	2.175	13.360
Col. 3	15	0	202.154	19.002	19.002	40.755	235.490
Col. 4	15	0	187.867	11.005	11.005	23.603	154.500
Column	**Max**	**Min**	**Median**	**25%**	**75%**	**Skewness**	**Kurtosis**
Col. 1	35.080	0.000	20.070	14.450	29.275	−0.542	−0.289
Col. 2	21.540	8.180	12.630	12.122	15.858	0.730	0.230
Col. 3	346.190	110.700	204.140	140.082	247.917	0.671	−0.444
Col. 4	251.000	96.500	196.000	161.000	220.375	−0.553	0.0238
Column	**K-S Dist.**	**K-S Prob.**	**SWilk W**	**SWilk Prob.**	**Sum**	**Sum of Squares**	
Col. 1	0.116	0.745	0.938	0.360	314.720	8240.871	
Col. 2	0.172	0.263	0.919	0.188	207.640	3090.289	
Col. 3	0.135	0.587	0.929	0.264	3032.310	688,817.446	
Col. 4	0.109	0.788	0.972	0.883	2818.000	554,841.000	

Col. 1—Char Yield, Col. 2—THR, Col. 3—HRC, Col. 4—TIME1.

Based on the *q* values from the Student-Newman-Keuls test, presented in Table 6, it can be seen that there are no statistically significant differences (p>0.05) between the HRC values (column 3) and the TIME1 values (column 4).

The data from the databases created based on thermogravimetric analysis in nitrogen and air, respectively, using the MCC technique for CHo-waste binary mixtures were normalized using Equation (2)

$$\text{Normalized value} = \frac{Y - Y_{\min}}{Y_{\max} - Y_{\min}} \quad (2)$$

where Y represents the amount of residue (%) in air and nitrogen, respectively, and Ts values in air and nitrogen. For MCC Y, Time 1 is the time after the first peak appears in the HRR = *f*(time) graph, THR is the total amount of heat energy released, and HRC is the heat release capacity. These were used to construct the radar graphs in Figures 1 and 2, specifying that the representation (1-normalized value) was used for the amount of residue, for T_s and TIME1, because we were interested in low values in these cases.

Table 6. Results of the Kruskal-Wallis test of mixtures with the Cho—MCC technique.

Comparison	Diff. of Ranks	q	$p < 0.05$
Col 3 vs. Col 2	516.000	7.629	Da
Col 3 vs. Col 1	395.000	7.765	Da
Col 3 vs. Col 4	11.000	0.323	Nu
Col 4 vs. Col 2	505.000	9.928	Da
Col 4 vs. Col 1	384.000	11.262	Da
Col 1 vs. Col 2	121.000	3.549	Da

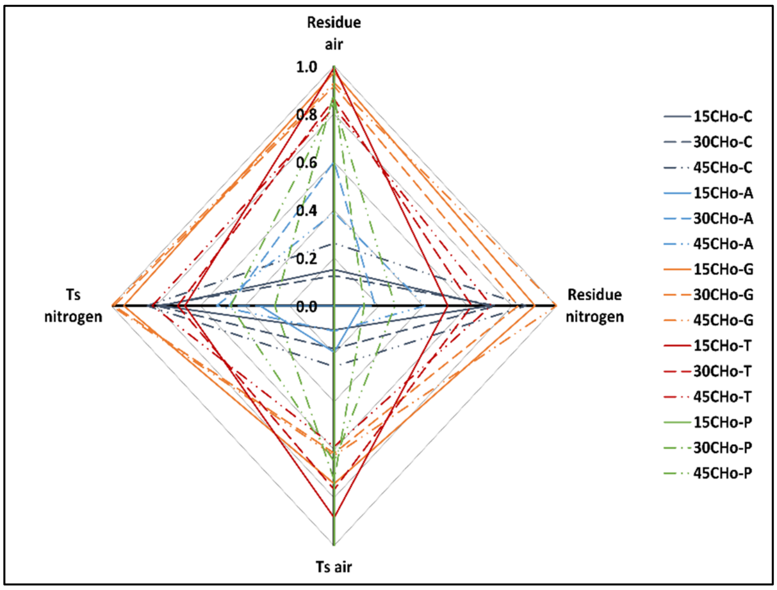


Figure 1. Evaluation of the synergistic effect for CHo-waste mixtures by thermogravimetric analysis.

The results presented in Figure 1 obtained for mixtures with CHo and railway beam waste (CHo-G) and textiles (CHo-T), respectively, show the best thermal performance in both working atmospheres, indicating efficient degradation and reduced residue formation. At the opposite end of the spectrum, an antagonistic effect was observed for the binary mixtures (CHo-P) and (CHo-C), which showed increased thermal stability and a higher amount of residue in the air, indicating limited degradation in the presence of oxygen. The CHo-A mixtures exhibited intermediate thermal behavior, with more efficient degradation in an inert atmosphere (nitrogen). In this atmosphere, Ts was lower and the amount of residue was smaller, suggesting efficient pyrolysis. In air, the behavior was more inert, with higher Ts values and increased residue, indicating the formation of refractory or incompletely oxidizable compounds from the tire structure. The best results, a synergistic effect, were obtained for CHo-G mixtures due to favorable interactions between the organic compounds in the algal biomass and the components of the treated wood (possibly thermally catalyzed by oxygen in the atmosphere), favoring more complete decomposition of the solid material. A more pronounced synergistic effect is also evident in the case of 15CHo-A and 15CHo-P mixtures if the thermogravimetric analysis is performed in an inert atmosphere, nitrogen. These results are consistent with those reported by other authors in the literature [8,17–19]. Recently, Xing et al.

[20] have highlighted synergistic effects in the pyrolysis process of binary mixtures: biomass-polyethylene terephthalate (PET) and biomass-polypropylene (PP) through thermogravimetric analysis. The authors demonstrated that this synergistic effect stems mainly from the interaction between the volatile substances in plastic and biomass. The maximum synergistic effect, measured by comparing the experimental and theoretical thermogravimetric curves, was achieved for the binary mixture of biomass (cane root): PP in a 1:3 ratio, demonstrating faster and more efficient degradation in the thermal stages, respectively, resulting in the lowest amount of residue and high degradation efficiency [20]. Mishra and his colleagues [9] also used thermogravimetric analysis in nitrogen to evaluate the thermal decomposition of binary mixtures of Samanea saman seeds and PET in different ratios (1:1, 3:1, and 5:1). The authors demonstrated that the 3:1 ratio indicates the strongest synergistic effect, i.e., a lower activation energy (Ea) compared to the individual materials (seeds or PET), facilitating the initiation of the reaction at lower temperatures and the intense release of volatile compounds [9]. Another study by Najaf et al. [10] investigated the thermal and kinetic characteristics of the co-pyrolysis of tea stems (TS) and polyethylene terephthalate (PET) using thermogravimetric analysis (TGA). The results showed that the co-pyrolysis of TS and PET exhibited both synergistic and antagonistic effects, depending on the temperature range and mixing ratio. It was found that the 75:25 (TS:PET) mixture generated the strongest synergistic effects [10]. Synergistic effects in the co-pyrolysis process of binary mixtures of *Chlorella pyrenoidosa* (CP) and polystyrene (PS) were highlighted by thermogravimetric analysis in nitrogen by Kong and his collaborators. The authors found that the CP:PS ratio of 1:1 generated the strongest positive synergistic effect, contributing to a decrease in activation energy and favoring decomposition at lower temperatures [11]. These results suggest that the observed synergistic effects arise from favorable interactions between volatile compounds released during pyrolysis and the solid matrix components, promoting faster and more complete decomposition. The differences observed between inert and oxidative atmospheres highlight the role of oxygen in enhancing or limiting thermal degradation. These findings are relevant for practical applications, as they can guide the selection of feedstock mixtures for thermal conversion processes, maximizing decomposition efficiency while minimizing residue formation. Overall, the thermal behavior trends observed in the mixtures provide insight into the mechanisms driving synergistic or antagonistic effects in co-pyrolysis, emphasizing the influence of material composition and reaction environment.

The radar chart in Figure 2 shows that CHo-P mixtures have the highest calorific potential (high HRC and THR), meaning that they burn almost completely and ignite early. These may be favorable in energy recovery applications. The CHo-T and CHo-G binary mixtures are the most advantageous in terms of ignition and residue quantity, but the THR and HRC values are moderate, making them suitable for applications where thermal stability and combustion control are priorities. CHo-A mixtures show a good balance between energy performance and complete degradation, being safer than CHo-P but more active than CHo-T or CHo-G. The most modest results were obtained for CHo-C binary mixtures, which do not excel in any of the parameters considered, offering neutral behavior in MCC, with reduced potential both in terms of energy and combustion control.

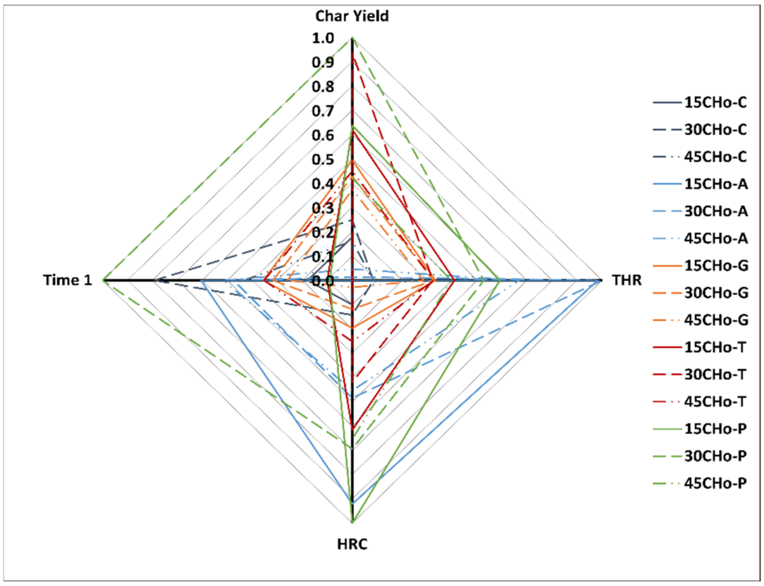


Figure 2. Evaluation of the synergistic effect for CHo-waste mixtures using the MCC technique.

By summing the normalized values calculated with Equation (2), the influence score was obtained, being graphically represented in Figure 3a for the thermal properties and in Figure 3b for the properties obtained by the MCC technique.

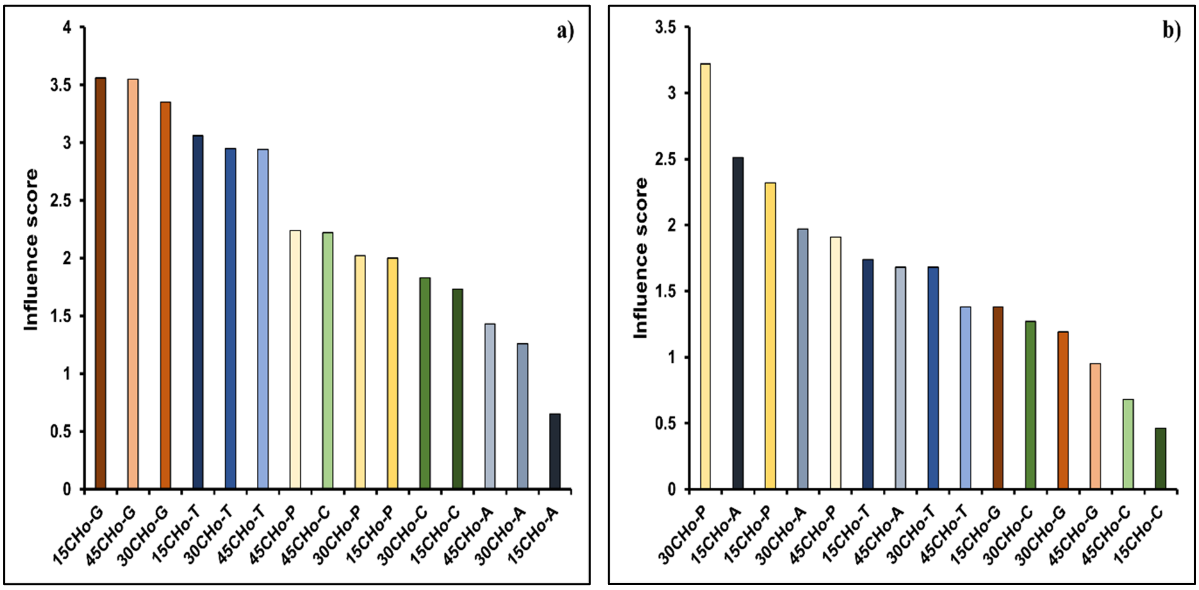


Figure 3. Influence score for binary mixtures with CHo (**a**) thermogravimetric analysis, (**b**) MCC technique.

Figure 3a shows that the series of binary mixtures between the used beam and used *Chlorella vulgaris* exhibit the best results, with values ranging between 3.35 and 3.56, indicating efficient thermal behaviour, with low decomposition temperatures and a minimum amount of residues. This suggests a high potential for efficient thermal recovery. This suggests high potential for efficient thermal recovery, with faster and more complete pyrolysis. Mixtures with textiles (CHo-T) follow in terms of efficiency, while those with plastics (CHo-P) and cardboard (CHo-C) show moderate scores. The lowest scores are obtained by mixtures with tires (CHo-A), which may indicate slower thermal degradation and a higher amount of residue, aspects that are less favorable for thermal conversion. The lowest value is reported for the 15CHo-A mixture (0.65).

Using the MCC technique (Figure 3b), the highest value is reported for the 30CHo-P mixture (3.22), and the lowest value for the 15CHo-C mixture (0.46). Mixtures with textiles (CHo-T) and plastics (CHo-P) offer a good combination of thermal performance and high calorific value, making them suitable for rapid conversion in thermochemical processes. In contrast, CHo-A mixtures are less thermally efficient but have a high calorific capacity, making them suitable for direct energy recovery, with influence scores that place them in the top part of the ranking, as shown in the graph in Figure 3. The comparison between the thermal analysis and MCC-derived scores highlights the importance of combining multiple assessment techniques to identify optimal mixtures for energy recovery and controlled combustion. Overall, these results indicate that the mixture composition strongly influences both degradation efficiency and energy potential, providing valuable guidance for selecting feedstocks in practical thermochemical applications.

4. Conclusions

The study investigated the thermal behavior of binary mixtures formed from spent biomass of Chlorella vulgaris (CHo) with various types of waste, under oxidizing (air) and inert (nitrogen) atmosphere conditions, using TGA and MCC techniques.

The thermal behavior of the mixtures is strongly influenced by the nature of the waste and the type of working atmosphere. In air, mixtures with components specific to wood material (G) and algal showed more advanced decomposition and more efficient oxidation, with a reduction in the amount of residue. In nitrogen, the CHo-A and CHo-P mixtures exhibited efficient pyrolysis, characterized by lower Ts temperatures and reduced residues, indicating a more efficient thermal conversion of the organic fraction. The CHo-C and CHo-P mixtures generally exhibited more inert thermal behavior, with higher amounts of residue in the air atmosphere, suggesting the formation of refractory compounds or incomplete oxidation. However, CHo-P stood out with the highest values of calorimetric parameters (HRC and THR), indicating superior energy potential and suitability for energy recovery applications through controlled combustion.

The influence scores obtained based on normalized values (for residue, Ts, and MCC parameters) indicate that CHo-G mixtures are the most efficient in terms of thermal degradation and calorific behavior. These mixtures obtained scores between 3.35–3.56 for thermal behavior. The CHo-T and CHo-G blends are the most advantageous for applications requiring efficient combustion control through early ignition, low residue, and moderate thermal stability, while the Cho-C blends showed lower energy performance, being less favorable for energy conversion applications.

Future work will focus on evaluating thermal behavior of mixtures with other biomass or organic wastes, optimizing processing conditions, and exploring practical applications in the cement industry to enhance energy recovery and sustainability.

Author Contributions

L.-V.P.: conceptualization, methodology, software, visualization, original draft preparation; G.S.: data curation, original draft preparation, manuscript reviewing; I.C.: original draft preparation, manuscript reviewing; G.L.: conceptualization, methodology, software, visualization, original draft preparation. All authors have read and agreed to the published version of the manuscript.

Funding

This research received no external funding.

Institutional

Not applicable.

Informed Consent Statement

Not applicable.

Data Availability Statement

Not applicable.

Conflicts of Interest

The authors declare no conflict of interest. Given the role as editorial board member, Gabriela Soreanu had no involvement in the peer review of this paper and had no access to information regarding its peer-review process. Full responsibility for the editorial process of this paper was delegated to another editor of the journal.

Use of AI and AI-Assisted Technologies

No AI tools were utilized for this paper.

References

1. Silva, F.C.N.; Flórez-Orrego, D.; de Oliveira Junior, S. Exergy assessment and energy integration of advanced gas turbine cycles on an offshore petroleum production platform. *Energy Convers. Manag.* **2019**, *197*, 111846. https://doi.org/10.1016/j.enconman.2019.111846.
2. Kohlhepp, P.; Harb, H.; Wolisz, H.; et al. Large-scale grid integration of residential thermal energy storages as demand-side flexibility resource: A review of international field studies. *Renew. Sustain. Energy Rev.* **2019**, *101*, 527–547. https://doi.org/10.1016/j.rser.2018.09.045.
3. Kamaruddin, N.A.B.; Ghani, W.A.A.K.; Hamid, M.R.A.; et al. Simulation and Analysis of Calorific Value for Biomass Solid Waste as A Potential Solid Fuel Source for Power Generation. *J. Appl. Sci. Eng.* **2023**, *26*, 163–173. https://doi.org/10.6180/jase.202302_26(2).0002.
4. Mukherjee, C.; Denney, J.; Mbonimpa, E.G.; et al. A review on municipal solid waste-to-energy trends in the USA. *Renew. Sustain. Energy Rev.* **2020**, *119*, 109512. https://doi.org/10.1016/j.rser.2019.109512.
5. Sanchez-Silva, J.M.; Ocampo-Pérez, R.; Padilla-Ortega, E.; et al. Pyrolysis Kinetics of Byrsonima crassifolia Stone as Agro-Industrial Waste through Isoconversional Models. *Molecules* **2023**, *28*, 544. https://doi.org/10.3390/molecules28020544.
6. Yao, Z.; Romano, P.; Fan, W.; et al. Probing pyrolysis conversion of separator from spent lithium-ion batteries: Thermal behavior, kinetics, evolved gas analysis and aspen plus modeling. *Case Stud. Therm. Eng.* **2024**, *63*, 105342. https://doi.org/10.1016/j.csite.2024.105342.

7. Gandhi, K.; Jaiswal, Y.; Suryawanshi, B.; et al. Co-pyrolysis behaviour of de-oiled mahua cake and waste LDPE using thermogravimetric analysis and artificial neural network. *Biomass Bioenergy* **2025**, *198*, 107870. https://doi.org/10.1016/j.biombioe.2025.107870.
8. Nawaz, A.; Razzak, S.A. Synergism, pyrolysis performance, product distribution and characteristics in the co-pyrolysis of date palm waste and polyethylene foam: Harnessing the potential of plastics and biomass valorization. *Carbon. Resour. Convers.* **2025**, *8*, 100312. https://doi.org/10.1016/j.crcon.2025.100312.
9. Mishra, R.K.; Sahoo, A.; Mohanty, K. Pyrolysis kinetics and synergistic effect in co-pyrolysis of Samanea saman seeds and polyethylene terephthalate using thermogravimetric analyser. *Bioresour. Technol.* **2019**, *289*, 121608. https://doi.org/10.1016/j.biortech.2019.121608.
10. Najafi, H.; Laye, Z.R.; Sobati, M.A. Deep insights on the Co-pyrolysis of tea stem and polyethylene terephthalate (PET): Unveiling synergistic effects and detailed kinetic modeling. *J. Environ. Chem. Eng.* **2024**, *12*, 113906. https://doi.org/10.1016/j.jece.2024.113906.
11. Kong, D.; Wang, S.; Wang, Y.; et al. Co-pyrolysis of Chlorella pyrenoidosa and polystyrene: Kinetics and product distributions. *J. Energy Inst.* **2025**, *120*, 102109. https://doi.org/10.1016/j.joei.2025.102109.
12. Anton, C.; Curteanu, S.; Lisa, C.; et al. Machine learning methods applied for modeling the process of obtaining bricks using silicon-based materials. *Materials* **2021**, *14*, 7232. https://doi.org/10.3390/ma14237232.
13. Donohue, J.M.; Aczel, A.D.; Freund, J.E.; et al. Complete Business Statistics. *Am. Stat.* **1993**, *47*, 309. https://doi.org/10.2307/2685296.
14. Postolache, L.-V.; Soreanu, G.; Cretescu, I.; et al. Alternative energy sources from wastes and microalgae Chlorella vulgaris used for the capture of atmospheric CO_2 in the production of cement. *Mater. Today Sustain.* **2025**, *31*, 101175. https://doi.org/10.1016/j.mtsust.2025.101175.
15. Kumar, G.; Banerjee, R.; Singh, D.K.; et al. Arnaw, mathematics for machine learning. *J. Math. Sci. Comput. Math.* **2020**, *1*, 229–238. https://doi.org/10.15864/jmscm.1208.
16. Fisher, M.J.; Marshall, A.P. Understanding descriptive statistics. *Aust. Crit. Care* **2009**, *22*, 93–97. https://doi.org/10.1016/j.aucc.2008.11.003.
17. Chen, B.; Xie, D.; Jiang, Y.; et al. Co-pyrolysis of corn stalk and high-density polyethylene with emphasis on the fibrous tissue difference on thermal behavior and kinetics. *Sci. Total Environ.* **2024**, *957*, 177847. https://doi.org/10.1016/j.scitotenv.2024.177847.
18. Nawaz, A.; Razzak, S.A. Co-pyrolysis of biomass and different plastic waste to reduce hazardous waste and subsequent production of energy products: A review on advancement, synergies, and future prospects. *Renew Energy* **2024**, *224*, 120103. https://doi.org/10.1016/j.renene.2024.120103.
19. Tee, M.Y.; Wang, D.; Wong, K.L.; et al. Investigating waste valorization potential through the co-pyrolysis of waste activated sludge and polyethylene terephthalate: Analysis on thermal degradation behavior, kinetic properties and by-products. *Energy Convers. Manag.* **2025**, *325*, 119412. https://doi.org/10.1016/j.enconman.2024.119412.
20. Xing, B.; Hu, Y.; Wang, S. Study of synergistic effects in co-pyrolysis of biomass and plastics from the perspective of phase reactions. *J. Anal. Appl. Pyrolysis* **2025**, *186*, 106951. https://doi.org/10.1016/j.jaap.2025.106951.