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Pyrolysis Kinetic Parameters Study on Agro-Industrial Residues

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This study aims at investigating the pyrolysis kinetic parameters of hot pepper waste with a comparative analysis against tomato pomace; a material previously explored in the literature. The biomasses are air-dried, crushed, sieved to a mesh size of 500–630 µm, and then subjected to proximate and ultimate analyses. Kinetic parameters are determined using the Coats-Redfern model revealing activation energies (Ea) for hot pepper ranging from 11.79 to 27.17 kJ·mol^{-1}, while tomato pomace ranged from 11.00 to 23.92 kJ·mol^{-1}. The thermodynamic analysis has indicated that tomato pomace has lower enthalpy (ΔH: 1.55–14.47 kJ·mol^{-1}) and Gibbs free energy (ΔG: 239.42–264.48 kJ·mol^{-1}) compared to hot pepper (ΔH: 2.34–17.72 kJ·mol^{-1}; ΔG: 238.96–266.32 kJ·mol^{-1}) indicating less energy requirements and more favorable reaction conditions for its thermal degradation. However, the hot pepper structural stability results in a higher fixed carbon content making it ideal for biochar production, while tomato pomace exhibits higher reactivity making it more suitable for syngas generation. These results can then support the optimization of pyrolysis reactor design.

1. Introduction

Biomass is known as the oldest source of energy used by humans and is now evolving to be one of the most promising sources of fuel for the future. This is motivated by several factors, among which are the increased need for energy security, the decline in fossil fuel utilization, environmental concerns, and the promotion of socioeconomic benefits (Venkatesan et al., 2020). Tomato and hot pepper are widely cultivated agricultural products with an annual production of approximately 316 thousand tons for tomatoes and 99 thousand tons for hot peppers from greenhouse cultivation alone (Aidat et al., 2023). Both biomasses are available year-round by altering the harvest. Specifically, tomato cultivation is conducted from spring to autumn, while hot pepper is cultivated from autumn to winter. This process generates massive quantities of tomato and hot pepper wastes, which are usually referred to as “tomato pomace” and “hot pepper waste.” These residues are known to be unstable materials and difficult to preserve, which is linked to their physicochemical composition, the presence of activating enzymes, and high moisture content (Rintu Banerjee, 2020).
Biomass can be valorized through thermochemical processes, pyrolysis and gasification, into electricity, heat, or biofuels (Sharma et al., 2022). In addition, such residues can be valorized by recovering bioactive compounds, cellulose and lignin, for use in various areas, such as cosmetics, food packaging, etc. (Bassani et al., 2020). Tomato wastes have been deeply studied from both experimental and simulation approaches. Tomato peels is used to produce bio-oil via pyrolysis at different operating conditions; the pyrolysis temperature ranged from 450 °C to 650 °C, and the heating rate was set in the range of 5–25 °C/min. Again, the bio-oil was used in a diesel engine (Midhun Prasad and Murugavelh, 2020). (Elkhalifa et al., 2022) studied pyrolysis on multiple vegetable wastes, such as tomato, cucumber, carrots, and their blends. Previous results have shown that blending different biomasses have a negligible impact on released CH_4 and H_2 gases but had a considerable impact on released CO_2 resulting in a reduction of CO_2 in the composition by 17.10%, 9.11%, and 16.79%, respectively, from the released pyro-gas. (Brachi et al., 2018) studied the effect of torrefaction on tomato peels by combining experiments with equilibrium modeling. It has been found that the torrefaction pretreatment provides only a marginal improvement in product gas quality. On the other hand, studies on hot pepper wastes are limited in this field. This study aims then to investigate the pyrolysis kinetic parameters of hot pepper waste

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to contrast it with tomato pomace, which has already been extensively studied in the literature. The present findings play a great role in the optimization of pyrolysis reactor design providing essential data for the heat and mass balance calculations of the process.

2. Material and Methods

The used biomasses for the Thermogravimetric Analysis (TGA) are available from a local industry located in Eastern Algeria with a non-uniform particle size distribution and shape. In line with previous experience and literature suggestions (Qian et al., 2013), the biomass is dried at 95°C for 24 hours. It is then ground and sieved to obtain a particle size in the range of 500–630 µm.

2.1 TGA analysis

TGA is performed on the two biomasses. The experiments are conducted under nitrogen flow (100 mL·min^{-1}). An initial sample mass of 15 mg is used for each TGA run, and to ensure consistent results, the analyses are repeated three times. A slower heating rate (e.g., 10°C·min^{-1}) allows for better heat transfer between particles (Demiral and Şensöz, 2006) enhancing particle breakdown and promoting effective biochar formation.

2.2 Kinetic model

The Coats-Redfern model is a commonly used method for determining kinetic parameters from single-heating-rate TGA data. It helps evaluate the validity of model-based kinetic analysis and identify the most appropriate reaction mechanism for biomass decomposition. This approach simplifies kinetic equations providing a fast estimation of activation energy and reaction order for studying biomass degradation.

$$\ln\frac{g(\alpha)}{T^2} = ln\frac{A \cdot R}{\beta \cdot E_a} - \frac{E}{R \cdot T} \quad (1)$$

$\frac{g(\alpha)}{T^2}$ and $\frac{1}{T}$ have a linear relation that can be used to determine the activation energy (kJ/mol) and the pre-exponential factor (s^{-1}), The Coats-Redfern (CR) model is based on various mechanisms reported in Table 1.

Table 1: reaction mechanism (Călin et al., 2024)

denotation	mechanisms	Integral form g(α)	equation
P2	2-Powerlaw	$\alpha^{\frac{1}{2}}$	(2)
P3	3-Powerlaw	$\alpha^{\frac{1}{3}}$	(3)
P4	4-Powerlaw	$\alpha^{\frac{1}{4}}$	(4)
P2/3	2/3-Powerlaw	$\alpha^{\frac{3}{2}}$	(5)
F1	I-order reaction	$-ln\,(1-\alpha)$	(6)
F2	II-order reaction	$1-(1-\alpha)^{-1}$	(7)
F3	III-order reaction	$[(1-\alpha)^{-2}-1]/2$	(8)
D1	1D diffusional	α^2	(9)
D2	2D diffusional	$(1-\alpha)ln\,(1-\alpha)+\alpha$	(10)
D3	3D diffusional	$1-(1-\alpha)^{1/3^2}$	(11)
D4	Ginstling–Brounsteindiffusional	$\left[1-\left(\frac{2}{3}\right)\alpha\right]-(1-\alpha)^{\frac{2}{3}}$	(12)

2.3 Thermodynamics

The thermodynamic properties—Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS)—are calculated based on the kinetic parameters of the most accurate reaction mechanisms. The relationships used for these calculations are as follows:

$$\Delta H = E_a - R \cdot T_p \quad (13)$$

$$\Delta G = E_a - R \cdot T_p \cdot \ln\left(\frac{k_b \cdot T_p}{h \cdot A}\right) \quad (14)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_p} \quad (15)$$

Where R is the ideal gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$), T_p implies the peak decomposition temperature (K), k_b designates the Boltzmann constant (1.38 10^{-23} $J \cdot K^{-1}$), and h denotes the Planck constant (6.63 10^{-34} $J \cdot s$).

3. Results and discussions

3.1 Biomass characterization

In Table 2, proximate analysis shows the content of moisture, fixed carbon, volatile matter, and ash. Hot pepper waste has more fixed carbon (15.3 ± 0.22%) than tomato pomace (12.28 ± 0.09%) which can contribute to its higher calorific value. These residues have similar ash contents (6.6 ± 0.12% and 6.05 ± 0.08%, respectively), but hot pepper has less volatile matter than tomato pomace (66.42 ± 0.4% vs. 73.10 ± 0.25%). High levels of volatile matter suggest that syngas (H_2, CO, CO_2, CH_4) is produced during conversion. The two biomasses have a moisture percentage lower than 12%; these wastes meet the pyrolysis and gasification standards which require that the biomass has less than 15% moisture content.

Table 2: Biomass Proximate analysis results

		Components %		
Biomass	Moisture	Fixed carbon[a]	Volatile matter	Ash
Hot pepper	11.64 ± 0.14	15.3 ± 0.22	66.42 ± 0.4	6.6 ± 0.12
Tomato pomace	8.57 ± 0.03	12.28 ± 0.09	73.10 ± 0.25	6.05 ± 0.08

[a] Fixed carbon%=100-moisture-ash-volatiles

Table 3, on the other hand, demonstrates that the ultimate analysis is used to evaluate the basic chemical composition of materials in terms of carbon, hydrogen, and nitrogen content. A simple analysis of data in Table 3 reveals that hot pepper waste has a slightly lower carbon content (42.13%) compared to tomato pomace (44.15%), while the hydrogen content is nearly the same for the two biomasses (5.83% and 5.96%, respectively). Nitrogen content is lower in hot pepper waste than in tomato waste. The high oxygen content (O) present in the results of the ultimate analysis in Table 3 is due to their lignocellulosic structure formed by C, O, H, and N bonds that constitute the hemicellulose, cellulose, and lignin—the main components of lignocellulosic biomasses. Since the energy content is related to the higher C and H amounts, the biomass with the lowest O:C ratio presented the highest HHV (High Heating Value). To sum up, the presented results in Tables 2 and 3 show consistency with the reported results in the literature (Molino et al., 2018) .

Table 3: Biomass Ultimate analysis and high heating value results

			Components %			
Biomass	Nitrogen	Oxygen [b]	Hydrogen	Carbone	Sulfur	HHV [$MJ \cdot kg^{-1}$]
Hot pepper	1.71±0.11	50.33±0.9	5.83±0.1	42.13± 0.72	-	16.91
Tomato pomace	1.97±0.04	47.92±0.37	5.96±0.04	44.15±0.25	-	17.85

[b] Oxygen%=100-carbon-hydrogen-nitrogen

In Figure 1 (a), the Thermogravimetric Analysis (TGA) curves for hot pepper and tomato biomass illustrate the mass loss percentage as a function of temperature, whereas in Figure 1(b), the Derivative Thermogravimetric (DTG) curves for the same materials show the rate of mass loss as a function of temperature to support the TGA discussion.

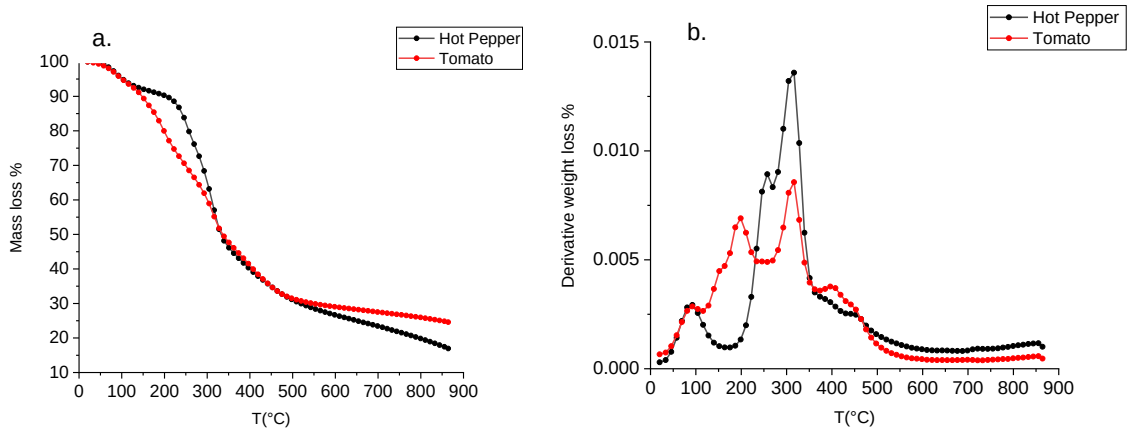

Figure 1: (a) is TGA profile for both biomasses, (b) is the DTG profile for both biomasses.

In the first stage (room temperature to 162°C), a minimal mass loss, which is attributed to the typical loss of water, is observed. This minimal loss indicates that the samples are effectively dried in the pre-treatment to an extent where only water in the physically adsorbed state remained to be removed (Mishra and Mohanty, 2020). This is confirmed by the derivative thermogravimetry (DTG) curves which show a distinct low-temperature peak corresponding to moisture removal. The second stage (200–380°C) represents the most significant mass reduction linked to the decomposition of hemicellulose and cellulose, which are the primary structural components of lignocellulosic biomass. Hemicellulose degrades at lower temperatures (200–270°C) followed by cellulose breakdown at slightly higher ranges (250–380°C) as supported by literature (El-Sayed et al., 2024). The DTG curves reflect this through two key peaks: a tomato biomass peak in the 200–300°C range followed by a more intense hot pepper peak directly indicating compositional variability between the biomasses. The heightened intensity of hot pepper's DTG peaks in both the hemicellulose (200–270°C) and cellulose (250–380°C) regions suggests a relative richness in these components compared to tomato pomace. Conversely, tomato exhibits less pronounced peaks in these ranges that is typically associated with elevated lignin proportions. These DTG trends align with the substantial mass loss observed in the TGA curves Figure 1 (a.) for the stage temperature range. The third stage, which is above 400°C, the mass loss rate declines significantly signaling the onset of lignin degradation. Lignin, being more thermally stable, decomposes gradually over a broad temperature range peaking near 850°C, which is consistent with prior studies (Boukaous et al., 2018). The delayed and prolonged degradation of lignin further supports the inferred compositional differences: tomato pomace with its hemicellulose/cellulose peaks likely retains a greater lignin fraction relative to hot pepper waste. The DTG curves mirror this behavior displaying broad and low-intensity slopes beyond 400°C due to lignin's prolonged degradation. This extended mass loss is also evident in the TGA data Figure 1 (a.) underscoring the complementary nature of TGA and DTG in characterizing thermal stability and compositional variations between biomasses.

3.2 Kinetic model analysis

Table 4 demonstrates the kinetic parameters derived from the Coats-Redfern model for the tomato pomace and hot pepper waste decomposition. The model relies on the linear relationship between $\frac{g(\alpha)}{T^2}$ and $\frac{1}{T}$ to calculate the activation energy (E_a) and pre-exponential factors (A).

Table 4: Kinetic properties of both biomasses evaluated with various reaction mechanisms.

Biomass	Mechanism	Ln A(s^{-1})	E_a (kJ·mol^{-1})	R^2
Hot pepper	F1	27.81	12.35	0.91
	D1	27.35	24.69	0.92
	D2	27.73	27.17	0.93
	D3	30.13	11.79	0.90
Tomato	F1	27.46	11.87	0.95
	D1	27.40	20.94	0.87
	D2	27.28	23.92	0.91
	D3	29.84	11.00	0.93

As shown in Table 4, activation energy (E_a) for hot pepper is between 11.79 and 27.17 kJ·mol^{-1} where the D2 mechanism shows the best value of the correlation coefficient (R^2=0.93) suggesting that this mechanism best describes the reaction kinetics for hot pepper pyrolysis. As for tomato pomace, it exhibits slightly lower activation energies ranging from 11.00 to 23.92 kJ·mol^{-1} with the F1 mechanism showing the highest R^2 value (0.95). These findings indicate that slightly less energy is required for its thermal decomposition of tomato pomace compared to hot pepper following the same mechanism. The pre-exponential factors (A) are higher for tomato pomace across in F1 and D3 mechanisms indicating a greater frequency of effective molecular collisions during its pyrolysis. The energy needed for activation in this case, however, minimizes molecular speed in reaction rates with respect to hot pepper while pyrolyzed at the same temperature. Most mechanisms are characterized with high R^2 values confirming that the Coats-Redfern model is suitable for describing pyrolysis kinetics of both biomasses.

In Table 5, the enthalpy change (ΔH) represents the energy required to initiate thermal decomposition. Hot pepper waste exhibits higher ΔH values (2.34–17.72 kJ·mol^{-1}) compared to tomato pomace (1.55–14.47 kJ·mol^{-1}) suggesting that hot pepper requires slightly more energy input for its thermal decomposition especially for mechanism (D2). These differences are consistent with the higher fixed carbon content and the structural stability of hot pepper which requires more energy to break its chemical bonds.

The Gibbs free energy (ΔG) values for both biomasses are positive, which means the reactions are non-spontaneous under the studied conditions. Tomato pomace constantly shows a few lower ΔG values (239.42 to 264.48 kJ·mol^{-1}) than hot pepper (238.96 to 266.32 kJ·mol^{-1}) indicating that its reactions are slightly more thermodynamically favorable. The entropy changes (ΔS) are negative for both biomasses signifying a reduction in system disorder during decomposition. However, the indifferent negative values of ΔS for tomato pomace (−0.20 to −0.23 kJ·mol^{-1}·K^{-1}) compared to hot pepper (−0.19 to −0.23 kJ·mol^{-1}·K^{-1}) suggest that the decomposition products of tomato are less ordered. This difference might be caused by the variations in the chemical composition and reaction mechanisms of the two biomasses.

Table 5: thermodynamics properties of both biomasses evaluated with various reaction mechanisms.

Biomass	Mechanism	ΔH (kJ·mol^{-1})	ΔG (kJ·mol^{-1})	ΔS (kJ·mol^{-1}·K^{-1})
	F1	2.9	244.04	-0.21
	D1	15.24	238.96	-0.19
Hot pepper	D2	17.72	239.85	-0.19
	D3	2.34	266.32	-0.23
	F1	2.42	239.49	-0.20
Tomato	D1	11.49	239.42	-0.20
	D2	14.47	238.97	-0.19
	D3	1.55	264.48	-0.23

4. Conclusion

This study confirms the potential of tomato pomace and hot pepper wastes as renewable energy sources through thermal degradation. The activation energy and pre-exponential factors highlight significant differences in their thermal decomposition behaviors. Tomato pomace, with slightly lower activation energy and a slightly higher pre-exponential factors, demonstrates faster reaction rates and higher reactivity making it suitable for syngas generation. On the other hand, hot pepper, characterized by higher structural stability and fixed carbon content, is ideal for biochar production. Accordingly, the research findings can contribute to the optimization of pyrolysis reactor design and provide essential data for the heat and mass balance calculations of the process.

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