Biochar development from thermal TGA studies of individual food waste vegetables and their blended systems

Samar Elkhailifa¹ · Prakash Parthasarathy¹ · Hamish R. Mackey¹ · Tareq Al-Ansari^{1,2} · Omar Elhassan³ · Said Mansour³ · Gordon McKay¹

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Abstract

The amount of food waste that is generated all over the world is enormous. As food wastes are rich in nutrients and organics, they serve as a potential source for the generation of many value-added commodities and energy. In most countries, food wastes are predominately dumped in open lands or incinerated, along with other combustible materials such as municipal solid wastes, for the possible extraction of energy. However, these two modes of food wastes disposal are encountering more and more environmental, technical, and economical challenges. More recently, it has been realized that food wastes can be transformed into energy and value-added products, such as horticultural biochars, using thermochemical technologies such as pyrolysis and gasification. In the current research work, three selected food items, carrots, cucumbers, and tomatoes, have been studied using thermogravimetric analysis. The biochar analysis involves one single food item (carrot), one binary mixture (carrot + cucumber), and one ternary blend of carrot, cucumber, and tomato. Two heating rates were used in order to perform kinetic modeling studies using the Arrhenius and Coats-Redfern models. Since the production of the pyrolysis gases—for energy and chemicals production—is of major economic significance regarding the overall process viability, the TGA syngas for a single component, binary component and tertiary component systems were analyzed by TGA coupled mass spectrometry. The results of the gas analysis indicate an increase in hydrogen generation due to blending the food wastes.

Keywords Pyrolysis · Vegetable waste foodstuffs · Biochar · Single and multi-components · Kinetics · TGA-MS

1 Introduction

Solid wastes are generated enormously around the globe because of the fast-paced rates of urbanization and industrialization. Several factors contribute to the concern over the proper management of these wastes, including a limited number of landfills, environmental challenges, and public

awareness. People are consuming more and generating vast quantities of waste to achieve increasing living standards, while industries are booming to meet such demands. Consequently, these unsustainable patterns place pressure on the environment, which is already suffering, and serious action must be taken to reverse the damage and save the planet for future generations.

The use of thermochemical conversion techniques in converting waste to energy is gaining wide acceptance due to the many benefits resulting from the conversion of waste into energy, fuel, and other products [1–3]. In particular, biomass waste constitutes a source of energy that is both cheap and abundant [4]. Therefore, biomass conversion into energy requires a lot more attention. There are many routes that can be followed to achieve the benefits of waste to energy conversion. Pyrolysis, for instance, is a promising technique that needs more research in order to be commercialized and used on a larger scale [5]. This will enable concepts like sustainability and the circular economy to be employed and utilized more efficiently worldwide.

✉ Prakash Parthasarathy
prakrock@gmail.com

✉ Gordon McKay
gmckay@hbku.edu.qa

¹ Division of Sustainable Development, College of Science and Engineering, Hamad Bin Khalifa University, Qatar Foundation, Doha, Qatar

² Division of Engineering Management and Decision Sciences, College of Science and Engineering, Hamad Bin Khalifa University, Doha, Qatar

³ Core Labs, Qatar Environment and Energy Research Institute, Hamad Bin Khalifa University, Doha, Qatar

Biochar is a charcoal-like material that is full of benefits and is the result of the conversion of waste to products through the pyrolysis process [6]. Some of the applications of biochar include its use in agriculture in order to increase water retention and fertility of lands and soils, in addition to its use as a precursor for adsorbents like those used in water treatment [7]. The addition of biochar to the soil can reduce denitrification, thus resulting in less N_2O emissions [8]; furthermore, several researchers have reported that adding biochar to the soil can boost crop yields by improving soil cation exchange capacity, water retention capacity, nutrient retention capability, improving soil fertility, and enhancing soil microbial activity, and pH [9–11]. Hence, it is important to understand the processes used to produce such biochars and other products. This can be achieved by the application of thermogravimetric analysis (TGA). The application of TGA involves studying changes in materials and products by following patterns related to change in weight loss with respect to temperature and time.

Globally, tomato is the second most used vegetable after potato, while carrot and cucumber are among the top ten most consumed vegetables. According to FAOSTAT, about 182 million tonnes of tomato, nearly 75 million tonnes of cucumber and gherkin, and almost 40 million tonnes of carrot and turnip are produced worldwide [12]. Due to the massive consumption of carrots, cucumbers, and tomatoes worldwide, huge quantities of these vegetable waste materials are produced every year. Despite having a high moisture content, the above vegetables have a high volatile content, which makes them potentially useful as sources of energy. Hence, in this study, carrot, cucumber, and tomato are considered, and their potential as feedstocks for pyrolysis is investigated. Many researchers have used TGA to investigate the pyrolytic conversion of biomass waste and food waste [13–15]. Specific examples of biomass waste and food waste included bamboo cane [16], camel manure [17], sewage sludge [18], and fruit waste [19]. The vast quantities of food waste generated are a strong motivation to use them in waste to energy conversion owing to their unique properties. This is especially true if methods like pyrolysis are used to transform them [20, 21].

The thermal characteristics and pyrolysis behavior of many vegetable wastes have been investigated by researchers. Table 1 presents excerpts of previous studies on pyrolysis characteristics of some top consumed vegetable wastes.

The table indicates that studies on thermal behavior and pyrolytic characteristics of some widely consumed vegetables such as tomato, cucumber, and carrot are yet to be made. Hence, in this study, the characteristics of pyrolytic decomposition of tomato, cucumber, and carrot wastes using TGA have been investigated. The study also investigates the pyrolytic response of the vegetable wastes' binary (tomato + cucumber, tomato + carrot, and

cucumber + carrot) and ternary (tomato + cucumber + carrot) blends which are quite novel. To produce value-added products from lignocellulosic biomass through pyrolysis, large amounts of feedstock would be required, which means blended biomass—rather than a single type of biomass—would be required. In addition, feedstock blending has a significant impact on the distribution of pyrolysis products. The pyrolytic degradation kinetics of all combinations (individual vegetable wastes, binary, and ternary vegetable blends) are determined employing two single-heating rate models such as Arrhenius and Coats-Redfern (CR). The information on the thermal characteristics and pyrolytic decomposition kinetics will be helpful in the design of pyrolyzer systems and in the calculation of the heat and mass balance of the process.

2 Materials and methodology

The three vegetable materials investigated in this study are carrots (*Daucus carota subsp. Sativus*), cucumbers (*Cucumis sativus*), and tomatoes (*Solanum lycopersicum*). These raw materials have been studied as a single-component system (carrot), binary component system (carrots + cucumbers), and the ternary component system (carrots + cucumbers + tomatoes). Prior to the TGA, the binary and ternary mixtures of components were prepared and mixed in an equal proportion by weight. This enabled the study of the different interactions between the components.

Initially, the raw materials (i.e., cucumbers, carrots, and tomatoes) were first dried using a hot-air oven at a temperature of 140 °C for 24 h. Next, the dried sample was chopped into smaller chunks, which was followed by grinding them into finer particles as required for TGA. The TGA was carried out from room temperature to 800 °C at two different heating rates, namely 5 and 10 °C/min under an N_2 atmosphere (100 ml/min) employing the thermogravimetric analyzer (Discovery TGA 550, TA Instruments). As the purpose of the study is to produce biochar, the TGA experiments were performed at slow heating rates (5 and 10 °C/min). Additionally, slow heating results in effective heat transfer between particles, resulting in effective cracking/decomposition of particles. Approximately 7–18 mg of the raw materials was used for the thermogravimetric weight-change analysis. TGA was conducted by ramping the temperature up from room temperature to 100 °C using two different heating rates of 5 and 10 °C/min; keeping an isothermal condition at 100 °C for 10 min; ramping the temperature up to 800 °C using two different heating rates of 5 and 10 °C/min. Furthermore, the evolving gases were monitored using a mass spectrometer coupled to the thermogravimetric analyzer.

Table 1 Previous studies on pyrolysis behavior of vegetable wastes

Vegetable waste	Objective of the study	Conclusion	Reference
Potato peel (<i>Solanum tuberosum</i>)	The objective of the study was to pyrolyse potato peel and generate good quality bio-oil and biochar	The study reported that potato peel biochar possesses excellent adsorption capacity and hence can be used as a feedstock for pyrolysis to produce many commercial products	[22]
Cauliflower (<i>Brassica oleracea</i>), lettuce (<i>Lactuca sativa</i>), and coriander (<i>Coriandrum sativum</i>)	The aim of the work was to generate fuels from vegetable wastes	The study reported that the chars from the vegetable wastes have high heating values and hence can be readily used as solid fuels	[23]
Chinese cabbage (<i>Brassica rapa</i> subsp. <i>Pekinensis</i>)	The intention of the study was to investigate the pyrolysis and gasification behaviour of Chinese cabbage	The study asserted that Chinese cabbage could serve as a potential feedstock for both pyrolysis and gasification processes	[24]
Cauliflower leaves (<i>Brassica oleracea</i>) and Pea pod (<i>Pisum sativum</i>)	The focus of the study was to pyrolyse the vegetable wastes to produce biochar. The study also intended to assess the suitability of the biochar for soil amendment application	The study confirmed that the biochars can increase soil carbon and water retention and hence can function as excellent soil conditioners	[25]
Onion (<i>Allium cepa</i>) and garlic (<i>Allium sativum</i>) skin	The work aimed at recovering cellulose microfibrers from the skins of onion and garlic vegetables	The study endorsed that the skins of onion and garlic can be a sustainable source for biopolymer production	[26]
Red pepper (<i>Capsicum annuum</i>)	The intention of the study was to investigate the thermal decomposition kinetics of red pepper waste to evaluate its potential for use as a solid fuel	The study confirmed that red pepper char has a high heating value and hence can serve as a good solid fuel	[27]
Pea (<i>Pisum sativum</i>)	The focus of the study was to analyse the prospective of pea waste as a potential source for bioenergy production	The work corroborated that pea waste can be a sustainable source for producing bioenergy	[28]
Banana (<i>Musa balbisiana</i>) flower petal	The aim of the study was to investigate the pyrolysis decomposition behaviour of banana flower petals and to assess the prospects of using the waste as a source for bioenergy generation	The results of the study validated that vegetable waste can serve as a source for bioenergy production	[29]

2.1 Materials characterisation

The materials analysis methods used to characterize these raw materials are:—proximate analysis on a wet and dry basis, for volatile content, fixed carbon, and ash content; elemental or ultimate analysis on a dry and ash-free basis for carbon, hydrogen, sulfur, nitrogen, and oxygen by difference. The standard followed for the determination of moisture content was a procedure by Choi et al. [30]. The instrument used for the proximate analysis was a SDT 650 (TA Instruments) Thermal analyzer, and the standard used for the proximate analysis was ASTM D7582–12. The elemental analysis of the feedstocks was carried out using a Euro-vector Euro EA 3000 CHN elemental analyzer. The ultimate analysis was conducted in line with standard ASTM D 3176–8.

2.2 Kinetic analysis models

For the purpose of pyrolyzer design, a detailed understanding of the pyrolysis-activation mechanism is essential. The TGA technique enables the study of the pyrolysis and activation behaviors of biomass materials. The formation of char from biomass consists of pyrolysis under an inert gas atmosphere to disintegrate the cross-linkage between carbon atoms. Although various kinetic models have been established for the study of pyrolysis mechanisms and kinetic parameters using TGA [31–39], in the present study, the Arrhenius and CR kinetic models were employed. The Arrhenius model is used because it is simple and assists in determining the order of reaction as such. In addition, the model had been used to determine the slow pyrolysis kinetics of lignocellulosic biomass such as sugarcane bagasse, coconut, coir pith, groundnut shell, casuarina leaves [40], sawdust, rice husk, and wheat husk, [41]. The CR model, like the Arrhenius model, does not require more than one heating rate to calculate kinetics and is used in this study because of its simplicity. The model was selected for its success in determining the slow pyrolysis kinetics of biomasses such as pine sawdust, olive waste, date palm trunk, seaweed [42], hemicellulose of Camellia Oleifera shell [43], and dry kitchen wastes [44].

2.2.1 Arrhenius model

The theoretical background of the model is presented below:

The kinetics of the devolatilization (pyrolysis) process can be given by

$$\frac{-dX}{dt} = kX^n \quad (1)$$

where X represents weight fraction undergoing decomposition, k corresponds to the reaction constant, and n is the order of the reaction.

The X and k can be presented as below:

$$X = \frac{w - w_f}{w_0 - w_f} \quad (2)$$

where w_0 is the initial weight of the sample before pyrolysis decomposition, w is the weight of the sample at a particular time, while w_f is the final weight of the sample after pyrolysis decomposition.

$$k = Ae^{-RT} \quad (3)$$

where R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature (K).

Substituting the values of X and k in Eq. (1) gives the below equation:

$$\ln \left[\frac{-1}{w_0 - w_f} \frac{dw}{dt} \right] = \ln(A) - \left[\frac{E}{RT} \right] + n \ln \left[\frac{w - w_f}{w_0 - w_f} \right] \quad (4)$$

where $\frac{dw}{dt}$ is the rate of change in weight of the sample undergoing degradation?

Equation (4) takes the below form:

$$y = B + Cx + Dz \quad (5)$$

where y resembles $\ln \left[\frac{-1}{w_0 - w_f} \frac{dw}{dt} \right]$, x resembles $\frac{1}{T}$, and z resembles $\ln \left[\frac{w - w_f}{w_0 - w_f} \right]$.

While the constant B and coefficients of C and D correspond to

$$B = \ln(A), C = \left[\frac{-E}{R} \right], D = n \quad (6)$$

2.2.2 Coats-Redfern model (CR)

In general, the CR model is given by

$$\ln \left[\frac{g(\infty)}{T^2} \right] = \ln \left[\frac{AR}{\beta E} \right] - \frac{E}{RT} \quad (7)$$

While the reaction mechanisms of the CR model can be broadly classified into (i) based on the rate-determining reactions; (ii) based on reactions influenced by the diffusion of solids; (iii) based on the interphase transfer of products [44]. A few most common reaction equations and the functions of $g(\infty)$ in the CR model are presented in Table 2.

2.3 TGA-MS analysis

The TGA-MS analysis provides information on the thermal behavior of feedstocks as well as details on the distribution of products. A mass spectrometer (MS) makes use of differences in the mass-to-charge ratio of ionized molecules to identify species or components, and those mass-to-charge ratios are

Table 2 Reaction models of the CR model

Reaction mechanism	Reaction model	Abbreviation	Integral form of the model $g(\alpha)$	Equation
Based on rate determining reactions	One nucleus on the individual particle	F_1	$-\ln(1-\alpha)$	(8)
	Two nuclei on the individual particle	F_2	$(1-\alpha)^{-1} - 1$	(9)
	Three nuclei on the individual particle	F_3	$[(1-\alpha)^{-2} - 1]/2$	(10)
Based on reactions controlled by diffusion of solids	One-dimensional diffusion	D_1	α^2	(11)
	Two-dimensional diffusion (Valensi model)	D_2	$(1-\alpha)\ln(1-\alpha) + \alpha$	(12)
	Three-dimensional diffusion (Jander model)	D_3	$1 - (1-\alpha)^{1/3^2}$	(13)
	Three-dimensional diffusion (Ginstling–Brounshtein model)	D_4	$\left[1 - \left(\frac{2}{3}\right)\alpha\right] - (1-\alpha)^{2/3}$	(14)
Based on the interphase transfer of products	Contracting area	R_2	$1 - (1-\alpha)^{1/2}$	(15)
	Contracting volume	R_3	$1 - (1-\alpha)^{1/3}$	(16)

referred from the National Institute of Standards and Technology (NIST) database. Since it is unviable to detect all gas components in the syngas, only the H_2 , CH_4 , H_2O , and CO_2 gas components were analyzed, considering the below equation.

The gas components H_2 , CH_4 , H_2O , and CO_2 were analyzed, referring to atomic mass units (amu) 2 (H_2), 15, 16 (CH_4), 17, 18 (H_2O), and 44 (CO_2), respectively. The mass spectra of N_2 , C_2H_4 , and C_2H_6 have the same amu 28. Since the TG-MS analysis was conducted under an N_2 atmosphere, the data for C_2H_4 and C_2H_6 was not presented as N_2 would have disturbed the amu 28 [45].

2.3.1 Semi-quantitative gas analysis

Radojević et al. [45] proposed a new method for estimating the quantity of gas components present in syngas. Based on the method, the volumetric share per unit mass of the gas component is determined using the below equation.

$$v_i \left[\frac{m^3}{kg} \right] = \frac{1}{\beta} \frac{v_c}{m} \int_{T_1}^{T_2} \frac{IC_i}{IC_c} dT \quad (18)$$

where v_i represents the volumetric share of gas component ($m^3 \text{ kg}^{-1}$), β refers to the heating rate of pyrolysis process (K/min), v_c corresponds to the volumetric flow rate of carrier gas (ml/min), m denotes the mass of the feedstock sample used for the analysis (mg), IC_i refers to the peak ion current of the gas component (A), IC_c represents the ion current of the carrier gas (A) (usually the carrier gas has a constant ion current value), T_1 and T_2 are the lower and upper limits of the integral function, indicating the temperature range

used in the calculation. The term T_1 is the logarithm of ion current of gas component while T_2 is the temperature that corresponds to the peak ion current of the gas component.

3 Results and discussion

3.1 Materials characterization

Any study of biomass foodstuffs needs to describe the characteristics and properties of the raw materials. When it comes to food waste, an elemental analysis on a dry basis as well as the moisture content is needed. Moisture content becomes critical in thermal treatment studies because it can range from a few percent to over ninety percent, consuming over sixty percent of the heat energy in the thermal processes. The classical analyses for the three vegetables under consideration, namely, carrots, cucumbers, and tomatoes, are now presented.

3.1.1 Proximate analysis

Due to the extremely wide range of moisture contents depending on the source and processing methods utilized, the proximate analyses are presented on a dry basis. The moisture contents of the natural vegetables are 90.01 wt. %, 96.07 wt. %, and 94.72 wt. % for carrots, cucumbers, and tomatoes, respectively. Experiments were performed at least in triplicate to obtain three consistent values that were within $\pm 5\%$. The results of the proximate analysis of the three vegetable food wastes are presented in Table 3.

Table 3 Proximate analysis of the chosen vegetables (this study)

Vegetable food wastes	Components (*db)		
	Volatile matter (wt. %)	Fixed carbon** (wt. %)	Ash content (wt. %)
Carrot	85.28	9.05	5.67
Cucumber	69.76	28.21	2.03
Tomato	80.43	14.78	4.79

*db, dry basis; **calculated by difference.

3.1.2 Ultimate analysis

The results of the ultimate analysis of the three vegetables are presented in Table 4. The values are based on the average of three measured results for each sample falling within $\pm 6\%$. The ultimate analysis results of these vegetables reported elsewhere are also presented in the table.

3.1.3 Heating value

The higher heating values (HHV) of the foodstuffs is calculated based on the results of the elemental analysis using the correlation proposed by Channiwala and Parikh [49] which is given below:

$$HHV \left(\frac{kJ}{kg} \right) = 349.1C + 1178.3H + 100.5S + 103.4O - 15.1N - 21.1Ash \quad (19)$$

The above correlation is used since the composition of all elements are well within the allowable limits suggested by the researchers, i.e., *C*: 0–92%, *H*: 0.43–25%, *N*: 0–5.6%, *O*: 0–50%, *Ash*: 0–71%, *HHV*: 4745–55,345 kJ/kg. The obtained heating values of the vegetable wastes are compared with the heating values of other vegetable wastes (cauliflower [23], lettuce [23], coriander [23], banana flower [29], pea [28], potato peel [22]) (see Fig. 1).

It can be noted that the cucumber and tomato wastes have high heating values. The high heating values of the

Fig. 1 Heating values of vegetable food wastes

vegetable food wastes are due to their high carbon content and low ash and oxygen content. On the other hand, carrot waste exhibits a low heating value. The low heating value of the waste is because of its low carbon and high oxygen content.

3.2 TGA profiles and biochar yields

The TGA profiles at the two heating rates, 5 and 10 °C/min, are shown in Figs. 2, 3, and 4. The three profiles are for carrots only carrots and cucumbers binary blend and for carrots, cucumber, and tomatoes ternary blend in Figs. 2, 3, and 4, respectively. The TGA data are represented by the dashed lines. The differential thermal gravimetric, DTG, percentage mass losses are shown by the dotted lines and the percentage values on the left-hand scale. The mass quantities at each temperature can be abstracted from the TGA versus temperature curves and are presented in Tables 5 and 6 for the two heating rates at 5 and 10 °C/min.

Table 4 Elemental analysis results for the food samples dried for 24 h at 140 °C, using CHNS reactor

Foodstuff	Elemental composition (%) *dab					Reference
	Carbon	Hydrogen	Nitrogen	Oxygen**	Sulfur	
Carrots	41.50	5.43	1.41	51.66	-	This study
	40.30	5.60	1.30	52.80	0.31	[46]
	42.82	5.14	1.50	50.23	-	[47]
Cucumbers	56.73	6.48	3.94	32.85	-	This study
	57.36	6.82	3.63	32.06	0.13	[47]
Tomatoes	49.72	7.38	3.74	39.16	-	This study
	49.69	7.43	3.78	39.10	-	[48]
Carrots and cucumbers	49.31	5.99	2.50	42.20	-	This study
Carrots, cucumbers, and tomatoes	49.28	6.38	2.86	41.48	-	This study

*dab, dry and ash-free basis; **determined by difference.

Fig. 2 TGA/DTGA profiles for the carrots single component at 5 and 10 °C/min heating rates

Fig. 3 TGA/DTGA profiles for the carrots and cucumbers blend at 5 and 10 °C/min heating rates

Fig. 4 TGA/DTGA profiles for the carrots, cucumbers, and tomatoes ternary blend at 5 and 10 °C/min heating rates

Table 5 presents the mass yields at different temperatures on a dry mass basis by taking the moisture content into account and dividing by the dryness fraction for the mass values 5 °C/min. For a system at a fixed heating rate, the height of the first peak of the DTGA corresponds to moisture content (wt.%), which is then converted to the solid dryness fraction ($100 - \text{moisture content}$) and then used to divide the original mass yields to arrive at the corrected dry mass yields in Tables 5 and 6. The intention of these tables is to see if blending vegetable food wastes made any difference to the biochar yields.

The data in Table 5 show a steady decreasing trend in the mass fraction biochar product yield with increasing temperature for all three systems studied. The mass fractions showed, when multiplied by 100, represent the solid percentage yields. The single-component carrot has a higher yield at each temperature. This could be caused by the other two systems (binary and ternary) having moister and softer interiors associated with higher cellulose contents than carrots.

In Table 6, for the single component, the char yield at 800 °C is 0.457, the char yield for the binary is 0.415, and for the ternary component, the yield is 0.383. At 700 °C, the yields are 0.468, 0.436, and 0.406 for single, binary, and ternary systems, respectively. There is a slight trend showing a decrease in the mass yield with blending at both 700 and 800 °C, but at the heating rate of 5 °C/min, the differences in the yields are quite small. Considering the data at the higher heating rate of 10 °C/min and 800 °C, the single component carrot has the highest yield while the ternary component has the lowest yield.

As in the case of the lower heating rate, there is a slight trend in decreasing biochar formation with an increasing number of blended materials. In addition, the biochar yield is lower at the more rapid heating rate, which is well established in pyrolysis studies, so concluding there is more syngas and bio-oil produced with increased heating rate.

Figures 5 and 6 present the percentage char yields at different temperatures based on dry solids content at 5 and 10 °C/min, respectively.

Figures 5 and 6 demonstrate a slight difference in biochar yields at 600, 700, and 800 °C. The char yield for the single component is minimal at both heating rates, whereas it is high for the ternary system, as seen in the figures. The char yield of the binary component lies between the char yield of single and ternary components. In the case of 5 °C/min, the biochar yield of the single, binary, and ternary component was observed to be 44.2%, 43.0%, and 42.2% respectively, whereas, in the case of 10 °C/min, the biochar yield of the single, binary, and ternary component was observed to be 45.7%, 41.5%, and 38.3%, respectively. The biochar yields of

Table 5 Dry mass yields, as mass fractions, while taking the moisture content into account and dividing by the dryness fraction for 5°C/min

System	Dryness fraction	Temperature					
		300 °C	400 °C	500 °C	600 °C	700 °C	800 °C
Carrots	0.95	0.827	0.600	0.505	0.463	0.453	0.442
Carrots and cucumbers	0.94	0.787	0.585	0.500	0.479	0.450	0.425
Carrots, cucumbers, and tomato	0.93	0.785	0.570	0.484	0.450	0.424	0.408

Table 6 Dry mass yields, as mass fractions, while taking the moisture content into account and dividing by the dryness fraction for 10°C/min

System	Dryness fraction	Temperature					
		300 °C	400 °C	500 °C	600 °C	700 °C	800 °C
Carrots	0.94	0.826	0.596	0.500	0.479	0.468	0.457
Carrots and cucumbers	0.94	0.819	0.585	0.489	0.468	0.436	0.415
Carrots, cucumbers, and tomato	0.94	0.812	0.556	0.476	0.429	0.406	0.383

Fig. 5 Percentage char yields at different temperatures based on dry solids content at 5°C/min heating rate **Fig. 6** Percentage char yields at different temperatures based on dry solids content at 10°C/min heating rate

the current work are compared with biochar yields of other similar works in Table 7.

Table 7 Literature values for biochar yield at high temperatures

Biomass type	Heating rate (°C/min)	Biochar yield (%)	Temperature (°C)	References
Cereal	5	~20	700	[13]
Meat	5	~18	700	
Vegetable	5	~38	700	
Mixed food	5	~28	700	
Lignin–plastic mixture	10	~30	900	[50]
Lignin–bone mixture	10	~34	900	
Bone–plastic mixture	10	~38	900	
Lignin–bone–plastic mixture	10	~30	900	

3.3 Food waste decomposition mechanism

Inspection of Figs. 2, 3, and 4 at both heating rates, the total mass losses at 800 °C temperature is approximately 58–64%; however, the main volatilization fraction of the food waste biomasses is taking place between 180 and 510 °C. This significant volatile release may be assigned to the thermal decomposition of the three major food biomass constituents, namely: lignin, cellulose, and hemicellulose. These three constituent compounds have been well established as being responsible for this major mass loss during the pyrolysis process [51].

Furthermore, the presence of specific peaks can be observed in the DTGA results curves, representing the maximum reaction rates at both the heating rates. The initial peak can be seen in the region of 100–120 °C and is attributed to the evaporation of the moisture, for the current samples (because of the drying pretreatment), the mass loss is low in the region of 3–7%. The second DTGA peak can be observed in the region 250–270 °C for both heating rates 5 and 10 °C/min. This peak is principally attributed to the pyrolytic decomposition of hemicellulose. Several

other studies have reported in the scientific literature that hemicelluloses decompose in the 150–300 °C temperature range [52–55]. The third and final main peak is observed at 300–320 °C for both the heating rates. This peak is mainly attributed to cellulose itself, which generally undergoes degradation at quite high temperatures i.e. 300–400 °C [31, 52, 54]. In addition, the first biomass constituent to undergo decomposition at small temperatures is lignin itself, and its degradation occurs slowly at a very low reaction rate and proceeds right through the pyrolysis period until 800 °C with some peaking around 500 °C. Consequently, this implies that small sections of the second and third peaks on the DTGA curves are associated with the decomposition of lignin [56]. Nevertheless, there is quite a degree of similarity between curves generated at the two different heating rates applied in this study. The peaks themselves represent the same structure and composition, and the mass loss trends follow the same direction, particularly at the higher temperatures, but the quantitative amounts, although the differences are quite small, do represent a significant change in the relative quantities of product formation. This trend in product distribution change due to variations in the heating rate has also been reported in the literature [53, 57]. In the present study, it should be noted that the low heating rates were selected to investigate the slow pyrolysis, which has been shown to produce higher yields of product biochar.

3.4 Kinetic analysis

3.4.1 Arrhenius model

The TGA data are used to define Eq. (4), and the triplet kinetic parameters—pre-exponential factor, activation energy, and order of reaction were determined using a multiple linear regression equation in Microsoft excel. Only the kinetic parameters for the active pyrolysis zone (140–620 °C) were determined. The determined kinetic parameters for the food wastes at two different heating rates are presented in Table 8. The obtained R^2 values lie between 0.80 and 0.98, indicating the good fitness of the model. The R^2 values for all the runs were in the range of 0.80 and 0.98.

As can be seen from the table that the pre-exponential factor values for all the runs are in the range of 7.54×10^4 – 8.62×10^6 (s^{-1}). This low range of ($< 10^9 s^{-1}$) pre-exponential factor values indicates that the pyrolysis of the food wastes could be a surface reaction or closed complex reaction [58]. The activation energy values for the samples were between 15 and 26 kJ/mol. This low range of activation energy values signifies that the pyrolysis of the wastes would be simple and smooth. The reason for these low activation energy values could be due to their high cellulose and hemicellulose content and low lignin content. In general, the pyrolysis of cellulose and hemicellulose is simple and hence requires low activation energies while the pyrolysis of lignin is intricate, hence it needs high activation energies [40]. The order of reaction for all the wastes was between 0.75 and 0.89.

The obtained values of the kinetic parameters are compared with the kinetic values of other works. Mansaray and Ghaly [59] were one of the pioneers to employ the Arrhenius model for determining the pyrolytic kinetics of plant biomass wastes. The researchers used the model to determine pyrolysis kinetics of different varieties of rice husk. The estimated pre-exponential factor values were in the range of 1.97×10^{12} – 2.03×10^{15} (s^{-1}), while the activation energy values were between 142 and 189 (kJ mol^{-1}), and the orders of the reaction were between 0.70 and 0.83. Kumar et al. [60] employed the model to determine the kinetic parameters of corn stover pyrolysis. The triplet kinetic parameters for the active zone were in the range of 1.35×10^4 – 7.33×10^4 (s^{-1}), 57–63 (kJ mol^{-1}), and 0.74–0.73, respectively. Wu et al. [61] used the model to estimate the kinetic parameters of dairy manure pyrolysis. The pre-exponential factor, activation energy, and order of reaction for the active pyrolysis region were estimated to be 7.03×10^6 (min^{-1}), 93.63 (kJ mol^{-1}), and 6.37, respectively.

The kinetic parameters are primarily influenced by the nature of feedstocks, the composition of components present in the feedstocks, temperature range, and heating rate. Hence, a difference in the values of kinetic parameters is observed in all the studies.

Table 8 Kinetic parameters determined using Arrhenius model

Foodstuff	Heating rate (°C/min)	Pre-exponential factor (s^{-1})	Activation energy (kJ mol^{-1})	Order of reaction (–)
Carrots	5	5.44×10^5	25.88	0.88
	10	8.62×10^5	25.57	0.87
Carrots and cucumbers	5	7.54×10^4	17.25	0.75
	10	1.68×10^5	16.62	0.76
Carrots, cucumbers, and tomato	5	4.29×10^5	21.22	0.89
	10	2.89×10^5	15.81	0.80

3.4.2 CR model

In this model, plotting $\ln\left[\frac{g(x)}{T^2}\right]$ vs $\frac{1}{T}$ gives a slope from which activation energy (E) is calculated. Among the reaction models, only the models that are good fitting with the experimental values are considered, and the kinetic parameters obtained from them are provided in Table 9.

As can be seen that first-order reaction (F1) is the best-fitting model. This indicates that first-order reaction is dominant in the active pyrolysis zones of all chosen vegetable food wastes. The pre-exponential factor values for all the wastes were below 10^2 (s^{-1}), indicating that the pyrolysis of these wastes would undergo degradation smoothly without any complication. The obtained activation energy values ranged between 28 and 77 kJ mol^{-1} . The F1 mechanism exhibited the lowest E -value, while the D3 model demonstrated the highest E -value.

3.5 Thermodynamic properties

The kinetic parameters of the good fitting models were used to determine the thermodynamic properties such as enthalpy

(ΔH), Gibbs free energy (ΔG), and entropy (ΔS). The thermodynamic properties values were calculated using the following equations:

$$\Delta H = E - RT_p \quad (20)$$

$$\Delta G = E + RT_p \ln\left(\frac{k_b T_p}{hA}\right) \quad (21)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_p} \quad (22)$$

where R represents the gas constant having the value $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, T_p corresponds to the peak decomposition temperature (K), k_b denotes the Boltzmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$), and h stands for Planck constant ($6.63 \times 10^{-34} \text{ Js}$). The thermodynamic properties of the vegetable food wastes determined using different reaction mechanisms of the CR model are listed in Table 10.

ΔH is a state function of thermodynamic phenomena which indicates whether a system takes or emits heat. As can be noted from the table that ΔH values are between 26 and 72 kJ mol^{-1} . The positive values of ΔH for all the models

Table 9 Kinetic parameters of vegetable food waste samples determined using different reaction models

Vegetable food wastes	Heating rate ($^{\circ}\text{C}/\text{min}$)	Reaction order-based models	A (s^{-1})	E (kJ mol^{-1})	R^2
Carrots	5	First-order (F_1)	9.41×10^{-1}	37.85	0.90
		Two-way transport (D_2)	6.05×10^1	67.18	0.83
		Three-way transport (D_3)	1.21×10^2	75.56	0.88
		Ginstling–Brounshtein (D_4)	2.70×10^1	69.84	0.84
	10	First-order (F_1)	1.92	38.57	0.90
		Two-way transport (D_2)	1.18×10^2	68.11	0.81
		Three-way transport (D_3)	2.44×10^2	76.80	0.87
		Ginstling–Brounshtein (D_4)	5.34×10^1	70.86	0.83
Carrots and cucumbers	5	First-order (F_1)	3.42×10^{-1}	32.40	0.89
		Two-way transport (D_2)	9.34	56.58	0.80
		Three-way transport (D_3)	1.86×10^1	64.78	0.87
		Ginstling–Brounshtein (D_4)	4.18	59.17	0.82
	10	First-order (F_1)	4.98×10^{-1}	31.55	0.89
		Two-way transport (D_2)	1.07×10^1	54.88	0.80
		Three-way transport (D_3)	2.12×10^1	63.15	0.86
		Ginstling–Brounshtein (D_4)	4.76	57.49	0.82
Carrots, cucumbers, and tomatoes	5	First-order (F_1)	3.09×10^{-1}	32.49	0.90
		Two-way transport (D_2)	7.38	56.59	0.81
		Three-way transport (D_3)	1.50×10^1	64.90	0.87
		Ginstling–Brounshtein (D_4)	3.31	59.21	0.83
	10	First-order (F_1)	3.03×10^{-1}	28.97	0.90
		Two-way transport (D_2)	3.79	49.43	0.80
		Three-way transport (D_3)	7.95	57.78	0.87
		Ginstling–Brounshtein (D_4)	1.71	52.05	0.83

Table 10 Thermodynamic parameters of the vegetable food waste samples calculated using the CR model

Vegetable food waste	Heating rate (°C/min)	Reaction order-based models	ΔH (kJ mol ⁻¹)	ΔG (kJ mol ⁻¹)	ΔS (kJ mol ⁻¹ K ⁻¹)
Carrots	5	First order (F1)	32.92	186.76	-0.2594
		Two-way transport (D2)	62.25	195.57	-0.2248
		Three-way transport (D3)	70.63	200.55	-0.2191
		Ginstling–Brounshtein (D4)	64.90	202.20	-0.2315
	10	First order (F1)	33.57	186.22	-0.2536
		Two-way transport (D2)	63.11	195.16	-0.2194
		Three-way transport (D3)	71.80	200.21	-0.2133
		Ginstling–Brounshtein (D4)	65.85	201.88	-0.2260
Carrots and cucumbers	5	First order (F1)	27.55	183.57	-0.2677
		Two-way transport (D2)	51.73	191.73	-0.2402
		Three-way transport (D3)	59.93	196.58	-0.2345
		Ginstling–Brounshtein (D4)	54.33	198.23	-0.2469
	10	First order (F1)	26.56	185.62	-0.2648
		Two-way transport (D2)	49.89	193.64	-0.2394
		Three-way transport (D3)	58.16	198.48	-0.2336
		Ginstling–Brounshtein (D4)	52.50	200.29	-0.2461
Carrots, cucumber, and tomatoes	5	First order (F1)	27.60	185.70	-0.2686
		Two-way transport (D2)	51.69	194.27	-0.2423
		Three-way transport (D3)	60.01	199.10	-0.2363
		Ginstling–Brounshtein (D4)	54.32	200.81	-0.2489
	10	First order (F1)	24.00	162.16	-0.2310
		Two-way transport (D2)	44.45	192.73	-0.2479
		Three-way transport (D3)	52.81	197.40	-0.2418
		Ginstling–Brounshtein (D4)	47.08	199.30	-0.2545

signify that the energy is required from an external source to reach the transition state. This indicates that only small external energy is sufficient to pyrolyze these vegetables' food wastes. The ΔG values are positive and are consistent (162–202 kJ mol⁻¹). The positive values signify that the degradation phenomenon is an endergonic reaction. Negative ΔS values are observed for all the samples signifying the creation of activated complexes while small ΔS values indicate the slow reactivity of the samples.

3.6 Syngas analysis results

3.6.1 TGA-MS profiles

The TGA-MS profiles of carrot, carrot–cucumber, and carrot–cucumber–tomato are presented in Fig. 7.

As can be seen from Fig. 7, the peak release of H₂O and CO₂ occurs relatively at the same time, while the peak release of CH₄ takes place a little later, followed by the evolution of H₂. The release order of gases took place in the following order H₂O, CO₂, CH₄, and H₂, which is consistent with the observation of Ma et al. [62]. In general, the liberation of the above gases is a complicated phenomenon as

some gases evolve due to thermal degradation of feedstocks, some gases are adsorbed ones while the rest are released owing to secondary reactions among the product gases [63, 64]. It is significant to note that the ion-current intensities of H₂O and CO₂ are strong, indicating a high presence of hydroxyl groups and oxygen atoms in the selected food waste samples.

3.6.2 Pyrolysis stages

In general, based on the decomposition trend of the samples, the TG-DTG curves are classified into four stages: zeroth stage (<150 °C), the first stage (150–250 °C), the second stage (250–500 °C), and the third stage (> 500 °C). The zeroth stage corresponds only to the dehydration phase, wherein no gas products are evolved, and it can be assumed that no pyrolysis occurs in this stage. In the first stage, gases such as CH₄, C₂H₄, C₂H₆, and H₂O are liberated. No permanent gases such as H₂, CO, CO₂, and O₂ are produced in this stage. In the second stage, most gas products except H₂ are generated. The pyrolysis of biomass primarily occurs in this stage. In the third stage, biomass pyrolysis occurs with the production

Fig. 7 TGA-MS profiles: **a** carrot at 5 °C/min, **b** carrot at 10 °C/min, **c** carrot–cucumber at 5 °C/min, **d** carrot–cucumber at 10 °C/min, **e** carrot–cucumber–tomato at 5 °C/min, and **f** carrot–cucumber–tomato at 10 °C/min

of CO₂ and H₂. The interaction between CO₂ and H₂ also takes place in this stage. Table 11 presents the detected gas components and their respective pyrolysis stages. The table also presents the details of peak ion current and peak temperature of the gas components, which are very vital for the quantification of the gas components.

From Table 11, it can be noted that the temperature of H₂O peak lies between 202 and 332 °C, the temperature of CO₂ peak lies in the range 268–329 °C, the temperature of CH₄ peak is ranges between 267 and 524 °C, and the temperature of H₂ peak falls in the 569–654 °C temperature range. The observed temperature ranges indicate that the release of H₂O falls under the first and second stage of pyrolysis, the evolution of CO₂ falling under the second stage of pyrolysis,

the liberation of CH₄ belongs to the second and third stage of pyrolysis, while the discharge of H₂ belonging to the third stage of pyrolysis.

3.6.3 Effect of heating rate on the syngas components yield

Based on the equation, the volumetric compositions of H₂, CH₄, H₂O, and CO₂ components were calculated, and the effect of heating rate on the syngas components yield is illustrated in Fig. 8.

It can be seen from the figure that increasing heating rate from 5 to 10 °C/min produced an insignificant change in the H₂ yield of all feedstock samples.

Table 11 Evolved gas components and their respective pyrolysis stages

Food waste	Heating rate	Gas component	amu	Stage	Log10	Peak ion current (A)	Peak temperature (°C)
Carrot	5	H ₂	2	Third	−6.55	2.80×10^{-7}	630.19
				Second	−6.18	6.54×10^{-7}	495.84
		CH ₄	15	Second	−6.38	4.16×10^{-7}	323.27
				Second	−6.53	2.95×10^{-7}	271.00
				Third	−6.07	8.51×10^{-7}	509.46
				Second	−6.21	6.17×10^{-7}	322.19
		H ₂ O	17	Second	−6.34	4.52×10^{-7}	274.82
				Second	−5.74	1.82×10^{-6}	321.65
		H ₂ O	18	Second	−5.94	1.14×10^{-6}	268.25
				Second	−5.10	7.87×10^{-6}	321.11
		CO ₂	44	Second	−5.31	4.85×10^{-6}	268.84
				Second	−5.32	4.75×10^{-6}	322.73
				Second	−5.45	3.56×10^{-6}	269.92
Carrot	10	H ₂	2	Third	−6.32	4.77×10^{-7}	654.23
				Third	−5.97	1.07×10^{-6}	517.22
		CH ₄	15	Second	−6.22	6.07×10^{-7}	329.77
				Second	−6.46	3.50×10^{-7}	278.61
				Third	−5.86	1.38×10^{-6}	520.62
				Second	−6.03	9.40×10^{-7}	332.10
		H ₂ O	17	Second	−6.17	6.74×10^{-7}	279.69
				Second	−5.50	3.16×10^{-6}	332.02
		H ₂ O	18	Second	−5.71	1.94×10^{-6}	276.52
				Second	−4.85	1.42×10^{-5}	331.02
		CO ₂	44	Second	−5.07	8.49×10^{-6}	275.34
				Second	−5.08	8.34×10^{-6}	328.77
				Second	−5.21	6.17×10^{-6}	274.26
Carrot–cucumber	5	H ₂	2	Third	−6.61	2.45×10^{-7}	586.91
				Third	−6.23	5.95×10^{-7}	501.47
		CH ₄	15	Second	−6.43	3.70×10^{-7}	314.16
				Second	−6.59	2.56×10^{-7}	280.40
				Third	−6.08	8.25×10^{-7}	501.47
				Second	−6.25	5.68×10^{-7}	318.49
		H ₂ O	17	Second	−6.40	3.98×10^{-7}	267.82
				Second	−5.81	1.53×10^{-6}	318.49
		H ₂ O	18	Second	−6.05	8.83×10^{-7}	267.28
				Second	−5.19	6.40×10^{-6}	318.49
		CO ₂	44	Second	−5.42	3.76×10^{-6}	268.40
				Second	−5.76	1.72×10^{-6}	316.51
				Second	−5.88	1.33×10^{-6}	268.62

However, an elevation in heating rate brought about a decrease in the yields of CH₄. An increase in heating rate produced a decrease in H₂O yields of single and binary samples, while in the ternary sample an increase in H₂O yield is noted. An elevation in heating rate also produced a mixed trend in the yield of CO₂, i.e., a decrease in CO₂ yield in the case of single and ternary

samples and an increase in CO₂ yield in the case of the binary sample.

3.6.4 Effect of blending on the syngas component yield

The effect of blending on the syngas components yield at heating rates 5 and 10 °C/min is presented in Fig. 9.

Table 11 (continued)

Food waste	Heating rate	Gas component	amu	Stage	Log10	Peak ion current (A)	Peak temperature (°C)
Carrot–cucumber	10	H ₂	2	Third	−6.50	3.13×10^{-7}	569.45
				Third	−6.10	8.03×10^{-7}	509.59
		CH ₄	15	Second	−6.40	3.98×10^{-7}	325.37
				Second	−6.56	2.75×10^{-7}	276.40
				Third	−5.97	1.08×10^{-6}	520.43
				Second	−6.17	6.81×10^{-7}	332.03
				Second	−6.30	5.01×10^{-7}	270.90
		H ₂ O	17	Second	−5.69	2.03×10^{-6}	330.87
				Second	−5.92	1.21×10^{-6}	270.98
		H ₂ O	18	Second	−5.06	8.64×10^{-6}	327.62
				Second	−5.28	5.28×10^{-6}	270.90
		CO ₂	44	Second	−5.26	5.50×10^{-6}	327.62
				Second	−5.37	4.24×10^{-6}	273.15
Carrot–cucumber–tomato	5	H ₂	2	Third	−6.86	1.38×10^{-7}	615.00
				Second	−6.56	2.73×10^{-7}	499.03
		CH ₄	15	Second	−6.66	2.17×10^{-7}	319.23
				Second	−6.77	1.71×10^{-7}	269.16
				Third	−6.41	3.91×10^{-7}	503.90
		CH ₄	16	Second	−6.51	3.11×10^{-7}	315.41
				Second	−6.15	7.10×10^{-7}	318.10
		H ₂ O	17	Second	−6.36	4.37×10^{-7}	269.16
				Second	−5.53	2.96×10^{-6}	318.10
		H ₂ O	18	Second	−5.73	1.86×10^{-6}	270.25
				Second	−5.76	1.72×10^{-6}	316.47
		CO ₂	44	Second	−5.88	1.32×10^{-6}	269.16
Carrot–cucumber–tomato	10	H ₂	2	Third	−6.70	2.01×10^{-7}	654.74
				Third	−6.41	3.93×10^{-7}	505.80
		CH ₄	15	Second	−6.55	2.79×10^{-7}	325.99
				Second	−6.70	1.99×10^{-7}	281.28
				Third	−6.26	5.50×10^{-7}	523.26
				Second	−6.34	4.62×10^{-7}	328.07
		CH ₄	16	Second	−6.50	3.19×10^{-7}	274.76
				Second	−5.91	1.22×10^{-6}	327.07
				Second	−6.18	6.54×10^{-7}	273.68
		H ₂ O	17	First	−6.22	6.09×10^{-7}	202.83
				Second	−5.28	5.19×10^{-6}	325.99
				Second	−5.55	2.80×10^{-6}	273.68
		H ₂ O	18	First	−5.57	2.69×10^{-6}	202.83
				Second	−5.54	2.86×10^{-6}	323.74
				Second	−5.68	2.07×10^{-6}	273.66

Fig. 8 Effect of heating rate on the syngas component yield

It is interesting to note that at both heating rates, the H₂ yield is the highest for the ternary mixture followed by the single feedstock sample and then by the binary mixture. This indicates that the ternary mixture combination is encouraging the H₂ yield. At heating rate of 5 °C/min, the CH₄, H₂O, and CO₂ yields of a single feedstock sample are more than the binary and ternary mixtures. At a heating rate of 10 °C/min as well, apart from the H₂O yield, the yields of CH₄ and CO₂ are more than the binary and ternary mixtures. This indicates that the carrot favors more CO₂ and CH₄ production than cucumber and tomato upon pyrolysis. It is evident from the figure that the syngas yields of binary and ternary mixtures differ considerably and can be attributed to the differences in the cellulosic and hemicellulosic contents in the

binary and ternary mixtures. Different syngas compositions in binary and ternary mixtures signify that the interaction between carrot–cucumber and carrot–cucumber–tomato is different. It also indicates the synergistic effect of feedstock samples.

4 Conclusion

The current work focuses on the understanding of the pyrolysis process and the generation of biochars from food waste. According to the TGA results, the endothermal peaks of hemicellulose, cellulose, and lignocellulose degradation took place at ranges close to those reported in the literature studies, namely, 220, 315, and 505 °C, respectively. The biochar yields between 200 and 800 °C were in the range 82.7 to 40.8 w/w% and 82.3 to 38.3 w/w% at 5 and 10 °C/min, respectively. The biochar yields for the food waste blends were slightly lower than the yields for the individual food type. The gas analysis indicated that the ternary mixture produced the highest H₂ yield, followed by the single feedstock sample and then by the binary mixture. Different syngas compositions in binary and ternary mixtures signify that the interaction between carrot–cucumber and carrot–cucumber–tomato is different. Further research should focus on the product distribution and yields from blends of food wastes but also on blends of food wastes with other types of waste to study these synergistic effects.

Fig. 9 Effect of blending on the syngas components yield at heating rates: **a** 5 °C/min; **b** 10 °C/min

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Data availability The TGA and MS data file have been submitted as a separate file.

Code availability Not applicable.

Declarations

Conflict of interest The authors declare no competing interests.

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