Thermo-gravimetric and kinetic analysis of residues from biological treated food waste

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HIGHLIGHTS

- Lignin (69%), plastic (12%), bone (18%) residues are major components of biological treated food waste
- Maximum decomposition peaks of residues are; plastic (476^{o}C), Lignin (335^{o}C), and Bone (335^{o}C).
- Thermo-gravimetric analyzer was used to investigate the thermal conversion characteristics
- Low activation energy and synergy occurred at high-temperature phase (> 350^{o}C) among three mixtures

Abstract

In order to study the thermal behavior of residues from biological treated food waste composition, characterization of the residues was firstly investigated. The major components identified were lignin, plastics and bones. Further, investigations of pyrolytic characteristics using thermo-gravimetric analysis were studied on the single and mixed components. The experiments were conducted at a temperature range of 30^{o}C-900^{o}C at the heating rate of (10^{o}C/mins) in the presence of nitrogen atmosphere with a flow rate of 20mL/min^{-1}. Subsequently, kinetic analysis and mechanism were performed on thermo-gravimetric data of the single and co-pyrolysis components after thermal decomposition. The maximum weight loss temperature for bone and lignin occurred at 335℃, while plastic residues maximum decomposition peak temperature occurred at 476℃. Plastic in the mixtures displayed an increased maximum decomposition temperature of 500℃ where substantial complete decomposition occurred in the co-pyrolysis. The combination of the three residues indicated that experimental and calculated TG/DTG curves were in good agreement. However, the solid parts of the different components of the pyrolytic process of interaction do not follow the behavior of individual feedstock in the mixtures. It showed that low-temperature pyrolysis stage (<350 ℃) signifies no synergy among residues, while synergistic interactions was noticed with no inhibition of lignin and bone char residues at more than 350℃ on plastic. This phenomenon resulted in low activation energy requirements and residues mixtures suitability for disposal through pyrolysis process.

Key words -Thermo gravimetric analysis; biological treated food waste; kinetics; pyrolysis characteristics; activation energy; residues

Introduction

Municipal solid waste (MSW) generation has kept an increase of 8–10% annually in China (Zhang, et al., 2015; Yang, et al., 2012). Food waste constitutes the highest share in MSW, ranging from 50% to 70% (Tai et al. 2011). The huge proportions of food waste in MSW are often mixed with different waste compositions which are usually incinerated and land filled. Efforts in the present decades to solve these food waste problems in China enthused launching of food waste treatment pilot projects in 100 cities. The aforementioned projects mainly focus on collection, transportation, treatment and utilization of food waste (Wen et al., 2016). Considering the characteristics nature of food waste, further solutions for waste oil, fat, solid and liquid waste contents are being explored for optimal waste recycling and safe disposal.

Biological treatment process (aerobic and anaerobic digestion) such as composting and fermentation are among the highly adopted food waste treatment pilot projects to resolve the food waste challenges. This process yields compost for agriculture and bio-gas for energy utilization respectively. However, there is a fraction of about 30% of the total food waste materials (dry basis) remaining as non-compostable and difficult to degrade residues. These residues eventually were mainly disposed via landfill, open burning and incineration. These traditional disposal routes create growing pressure on waste management and consequent environmental impacts (e.g., soil degradation, GHG emissions and water pollution). In addition, it leads to wasteful resources exploitation.

In this context, pyrolysis techniques for residues of biological-treated food waste will be emphasized as sustainable route of disposal. Application of pyrolysis for the treatment of residues from anaerobic digestion and aerobic process is considered most applicable route to divert materials away from landfill and incineration. Pyrolysis represents a process of thermal degradation of waste in the total absence of air that produces recyclable products (Chen et., al, 2015). The process can be used for accomplishment of useful products of bio-oil, pyrogenic carbon (biochar), and biogas. It is imperative to mention that all these products have respective values for fuel, agriculture, energy utilization and carbon sequestration. Subsequently, in the next step of our research, pyrolysis products recycling and upgrades will be investigated through coupling with anaerobic digestion to provide for achievement of zero waste.

Pyrolysis and co-pyrolysis behavior with kinetics for municipal solid waste, raw food waste, sewage sludge and agricultural biomass had been extensively investigated (Titiloye, et al., 2013; Olajire, et al.,2014; Sajdak & Słowik,2014; Phuong, et al., 2015; Zhang, et al, 2015, Chang, et al.,2015; Lu, et al., 2013; Serio et al.,2012; Ni et al., 2006; Sun et al., 2015; Zhang, et al, 2016 ; Zhou, et al, 2015; Grycová, et al., 2016; Ward, et al.,2014).

Meanwhile, the residues considered in this study are mixtures of different materials such as bones, glass, metals, plastic and lignin. To fully comprehend the reactions and interactions that exist between the residues as single and mixed components. There was need to investigate the thermal mechanism and interactions between identified residues of bones, plastics, and lignin. Some reports published that both pyrolyzed plastics and biomass jointly, could possibly achieve significant synergistic effect for increase liquid products (Çepelioğullar & Pütün, 2014; Melendi-Espina, et al., 2015; Oyedun, et al.,2014; Paradela, et al.,2009; Sajdak, et al., 2015; Xue, et al.,2015). While some authors expressed contrary opinions about the significant results of co-pyrolysis of plastics and biomass. Some stated that the research failed to notice or does not found to a significant noticeable level synergistic effect on co-pyrolysis of plastics and biomass (Papuga, et al.,2013; Bhattacharya, et al.,2009; Jakab, et al.,2000; Li, et al., 2013).

Virtually, no sufficient literatures were found that focused on thermo gravimetric and kinetic analysis of these residues from bio-treated food waste. Hence, this might be the first endeavor extending research on pyrolysis behavior, kinetic analysis and mechanism of residues obtained from bio-treated food waste using the thermo-gravimetric method. Therefore, the major objectives will be (1) to conduct preliminary study of residues from bio-treated food waste; (2) to establish the thermal characteristics of the single components and mixtures by thermal gravimetric analysis; (3) to compare the experimental and simulated kinetic parameters; (4) to provide preliminary data and theoretical support for the next pyrolysis experiments and engineering applications of non-compostable residues obtained from bio-treated food waste.

Abbreviations

TGA	Thermo-gravimetric analysis
DTGA	Derivative Thermogravimetric Analysis
L	Lignin
B	Bone
P	Plastic
LB	Lignin-Bone
LP	Lignin -Plastic
BP	Bone – Plastic
LBP	Lignin-Bone-Plastic
MSW	Municipal Solid Waste

2. Materials and method

2.1 Sample Preparation

The residues from bio-treated food waste were collected from food waste processing plant in Beijing, China. The amount of 500g representative quantities of the residues were collected in triplicate and sorted into different waste streams, weighed and the data was recorded.

2.2 *Thermo-gravimetric analysis (TGA)*

The pyrolysis characteristics of the three single components and mixture were examined using a thermo gravimetric analyzer TG (Mettler Toledo –Stare System). A 150 mL Al_2O_3 crucible was loaded with 17mg sample and subjected to a heating rate of 10^{o}C/min from room temperature to 900^{o}C. Nitrogen was used as the TG gas with a flow rate of 20 mL/min so that the TG was conducted in an atmosphere without oxygen. Distribution of weight loss during the TG experiment enables us to carry out the thermo-gravimetric analysis (TGA) and the derivative thermo-gravimetric analysis (DTGA) of the residues.

2.3 *Kinetic theory*

Kinetic parameters such as activation energy and pre-exponential factor of the pyrolysis mechanism were derived based on the kinetic data obtained from thermo-gravimetric analysis. Generalizing, the rate of heterogeneous solid-state reactions can be generally described by the reaction 1 and 2.

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

$$\alpha = (m_o - m)/(m_o - m_f) \tag{2}$$

Where α is the conversion degree or reacted fraction of material decomposed as presented in equation 2, t is time, k indicates temperature-dependent constant while f(α) a function called the reaction model, which describes the dependence of the reaction rate on the extent of reaction.

Equation 3, presents mathematical description of the data from a single step solid state decomposition as usually defined in terms of a kinetic triplet. Where activation energy (E), Arrhenius parameters- pre-exponential factor (A), and an algebraic expression of the kinetic model in function of the fractional conversion f(α). This can be related to experimental data (where R is the ideal constant).

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{3}$$

The above rate expression in equation 3 can be transformed into a non-isothermal rate expression, describing reaction rate as a function of temperature at a constant β; To the sample reactions, the function of fractional conversion f(α) was expressed for $f(\alpha) = (1-\alpha)^n$, the kinetic equation may be described by equations as thus:

$$\frac{d\alpha}{dt} = \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \tag{4}$$

By rearrangement and integration of equation 4 ,following the Coats-Redfern approximation method which was also used recently by (Olajire, et al, 2014; Lu, et al., 2013,), equation (5) is obtained:

$$\int_0^{\alpha} \frac{d\alpha}{(1-\alpha)^n} = \left(\frac{A}{\beta}\right)\int_0^{T} e^{-E/RT}\,dT \tag{5}$$

For most temperature and activation energies RT/E<<1 and, therefore, equation (6) and (7) can be obtained from equation 5 for different n values as shown below:

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{\mathrm{AR}}{\beta\mathrm{E}}\left(1 - \frac{2\mathrm{RT}}{\mathrm{E}}\right)\right] - \frac{\mathrm{E}}{\mathrm{RT}}(n=1) \tag{6}$$

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{\left(T^2(1-n)\right)}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT}(n \neq 1) \tag{7}$$

Equation 6 or 7 may further be simply expressed as thus:

$$\mathrm{Y} = aX + b \tag{8}$$

Y: $\ln(-\ln(1-\alpha)/T^2)$ or $\ln[1-(1-\alpha)^{1-n}/(T^2 1-n)]$; X: 1/T ; a:-E/R; b:ln(AR /βE) (9)

Subsequently, for most values of E and the temperature range of pyrolysis, it could be shown that the expression in equation 6 and 8 are constant. Therefore, if $\ln(-\ln(1-\alpha)/T^2)$ (For n=1) or $\ln[1-(-\alpha)^{1-n}/(T^2 1-n)]$ (for n≠1) on the left side of equation 9 is plotted against 1/T on the right side of same equation 9, a straight line should be obtained if the process can be assumed as a first order reaction. Accordingly, the activation energy (E) and Arrhenius parameters - Pre-exponential factor (A) are being obtained from the slope and the intercept for different kinetic parameters pyrolysis stages respectively.

3. Results and discussion

3.1 Properties of residual matters

From the residues, three core components; plastic, lignin and bone were prepared with weight percentages of 18, 69 and 12 respectively as shown in Fig 1. Individual components of the samples prepared were used to conduct the TG, proximate and elemental analysis. Residues that constitutes 1% was screened out to avoid interference with thermal conversion process.

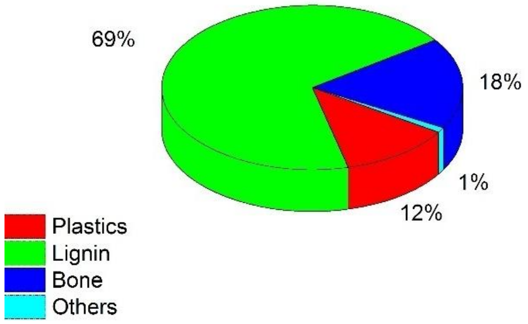

Fig.1. Physical compositions of residues from bio-treated food waste

The properties of the residues; lignin, bone and plastic was drawn from the ultimate and proximate analysis as shown in Table 1. The moisture content of residues is very low, not totally dried, thus, greatly reducing the energy demand for drying residues of high moisture contents. Plastic residues show the highest heating value of 29.93 MJ/kg with a high volatility and combustion when pyrolyzed alone. (Ellingham, et al., 2015; Olajire, et al., 2014) in their studies also reported similar characteristics on plastics higher volatiles and calorific values.

Table 1. proximate and elemental analysis for residues

Residues	Proximate analysis (wt.%)				Elemental analysis (wt.%)					HHV
	M_{ad}	A_{ad}	V_{ad}	FC_{ad}	C	H	O^*	N	S	MJ/Kg
Lignin	4.49	16.08	66.52	12.92	41.53	5.32	30.58	1.69	0.31	14.47
Plastic	1.68	7.53	83.35	7.44	61.06	7.89	19.37	1.27	0.41	29.93
Bone	4.82	38.95	52.89	3.35	29.17	4.09	20.17	3.29	0.32	11.90

N/B - ad: air dried; *: by difference; M_{ad}: Moisture Content; A_{ad}: Ash content; V_{ad}: Volatile content; FC_{ad}: Fixed carbon

The bones were found rich in inorganic substances such as Ca, Si, Fe and other mineral compounds, act as catalyst for pyrolysis. Hence, the residues with some of these metals can be assumed suitable for pyrolysis process. (Alhassan & Andresen., 2013; A. W. A. K.,1980) in their studies, reported that bone meal (BM) consist of high N, P and Ca content. Some of these elements are believed to exhibit catalytic effect during co-pyrolysis with biomass. According to elemental analysis in table 1: lignin substances; C: H: O ratio is 1:1.54: 0.55. plastic; C: H: O is 1:1.55:0.25, while bone residues; C: H: O ratio is 1:1.68: 0.52 Therefore, it can be deduced that higher oxygen content of lignin and bone matters easily lead to pyrolysis volatiles with low calorific values than plastic matters. Higher content of carbon and hydrogen in the plastic could improve the quality of pyrolysis bio-oil and gaseous products when mixed with lignin and bone with higher oxygen content. Hence, the three major fractions of residues from bio-treated food waste would be suitable for pyrolysis. Some authors discussed extensively the co-pyrolysis of biomass mixed plastics with their proximate analysis results (Abnisa et al., 2014).

3.2. Thermo-gravimetry analysis

3.2.1 Pyrolysis behaviors of single component

Pyrolytic characteristics of the three major components were investigated through thermo- gravimetric analysis (TG) and (DTG) for differential weight loss as shown in Figs 2(a,b). The TG and DTG curves for lignin, bone and plastic matters were subjected to pyrolysis temperature from 30^{o}C to the highest temperature 900^{o}C. This resulted to ultimate weight loss of 27.98 (wt.%), 43.54 (wt.%),13.32 (wt.%) respectively. Lignin and bone matters indicate maximum weight loss peaks at 335^{o}C for the two substances. Subsequently, noticeable small peaks were observed at 380^{o}C and 450^{o}C after the two substances maximum peak decomposition. The lignin had a wide temperature range between 200-450^{o}C which was also reported by Stefanidis, et al., (2014). However, considering the inherent structure and chemical nature of residues from bio-treated food waste, lignin consists of aromatic rings with various branches. The decomposition range cannot be specifically fixed because it varies over a long temperature range, therefore, a distinct weight loss peak is not discernible for lignin (Yang, et al.,2007; Yang, et al., 2015). Bone matters might have displayed similar characteristics because of long stirring during composting, enhancing lignin matters to adhere to bone surface as shown in Fig.2. In addition, biological and physical processes acting on the bone, its fats and protein contents combined with lignin matters might have promoted similar pyrolysis characteristics temperature. However, some authors reported that bone weight loss occurred in three successive temperature stages, the first below 200°C, the second between 200°C and 600°C and a third step between 700°C and 900°C (Ellingham, et al.,2015; Figueiredo, et al.,2010). Peak temperature at 720^{o}C was observed to be consistent in all samples thermal conversion process, though, with different peak intensities. (Ellingham et al.,2015; Mkukuma, et al.,2004; Figueiredo, et al.,2010) reported the last weight loss phase of bone is mainly due to the re-lease of CO_2 produced through the decomposition of carbonates and some inorganic substances. This of course, provides some significant insight to the distinct re-occurrence peak temperature at 720^{o}C in the TG/DTG analysis.

The decomposition of plastic residue could be divided into three distinct temperature ranges as shown in Figs..2 (a, b). Initial decomposition temperature step commenced at 250-335^{o}C, while the second temperature step was from 335-400^{o}C, and final step was from 400-500^{o}C. Though, small peak was noticed at 380^{o}C, while at 476 ^{o}C this temperature was maximum peak with very strong intensity. The initial decomposition temperature peak might be attributed to softening and gradual heat decomposition. These findings are similar to different reports on the peak temperatures for high density polyethylene (HDPE) -733K, polystyrene (PS) -678K and polypropylene (PP) above 400^{o}C (Zhou et al., 2015; Sajdak & Słowik, 2014).

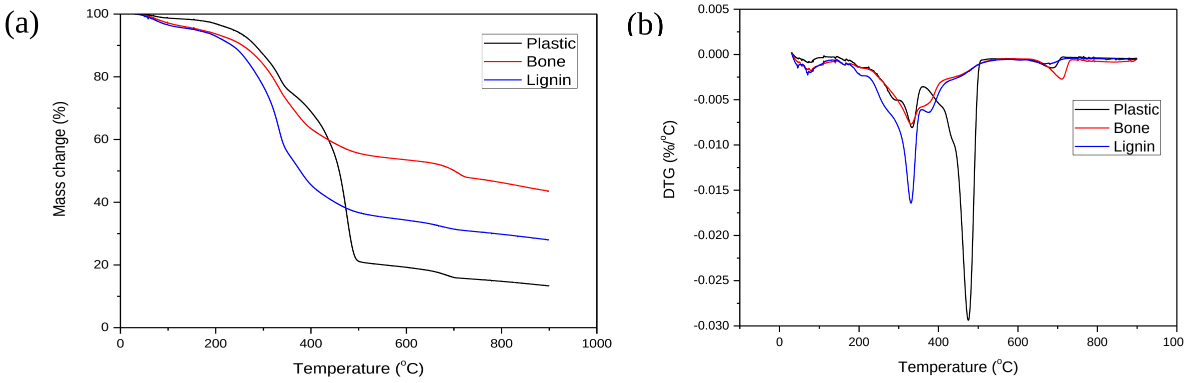

Fig.2. Three single residual matters (a) TG curves and (b) DTG curves

3.2.2 Pyrolysis behavior of mixed materials.

Different proportions of the residues (lignin, bone and plastic) displayed different thermal behavior, hence they were mixed to understand synergistic effect that might occur between them. If there exist no interactions in the thermal decomposition of the lignin, bone, and plastic mixtures, the pyrolysis characteristics will follow the behaviors of their parent materials in coherent manners. Different mixed ratio of lignin-bone, lignin-plastic, bone-plastic and lignin-bone-plastic was prepared in the percentage weight ratio of 8:2, 8:2, 6:4 and 69:18:12 to evaluate the synergy between respective mixtures. The experimental and calculated TGA and DTG curves are plotted as shown in Figs.3 (a, b, c, d) respectively.

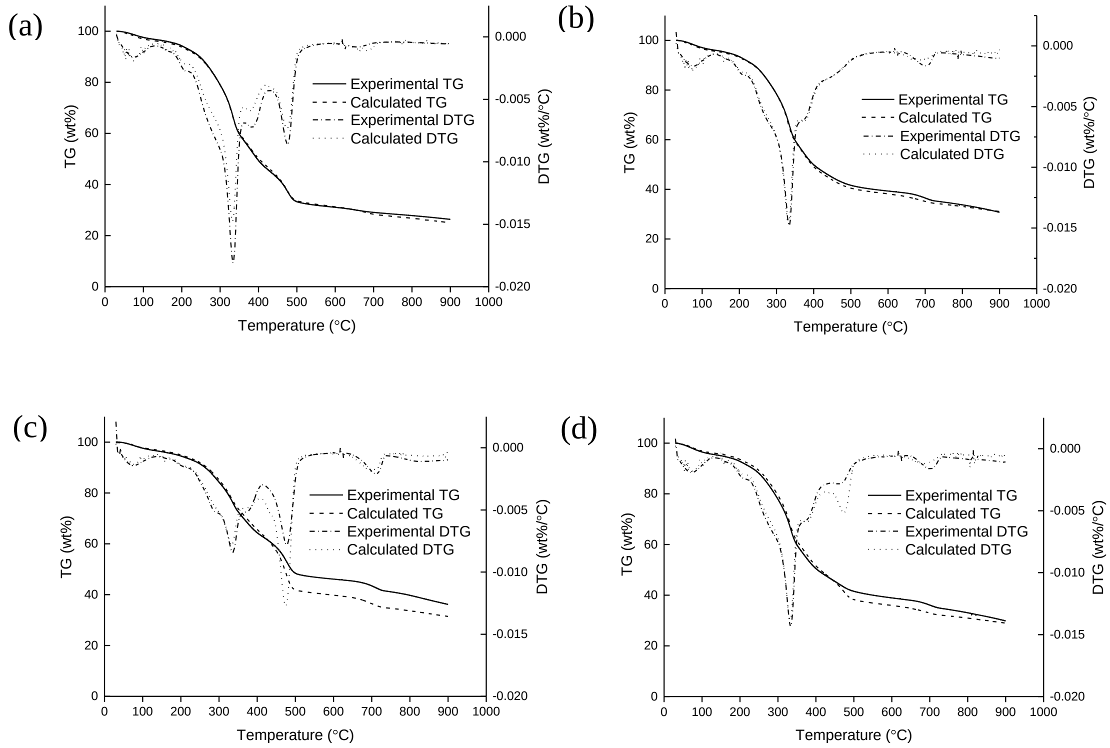

Fig.3. Experimental and calculated TG and DTG curves of (a) lignin mixed with plastic(b) lignin mixed with bone (c) bone mixed with plastic and (d) three samples mixed

The mixtures indicate consistent curve in the solid phase pyrolysis reaction system without substantial interaction or with little synergistic reactions in the gas phase. Synergy in the gas phase need to be studied in a specific pyrolysis experiments. In Figure (3a) lignin-plastics mixtures show that simulation experiment is greater than the absolute experimental value. This might be mainly due to cellulose and lignin low thermal decomposition temperature at the first peak, which does not interact with the thermal decomposition of plastic matters. This indicates that the pyrolysis thermal process was not significantly affected by the mixture of the two components. This was similarly reported on studies of co-pyrolysis of biomass and plastics (Li et al.,2013; Jakab, et al.,2000; Sharypov, et al.,2000; Brebu, et al.,2010; Chattopadhyay, et al.,2008). The structural characteristics of plastics might have hindered lignin biomass pyrolysis volatile gasses to escape, resulting in reduced weight loss rate. When the temperature reaches the decomposition point of the plastic, lignin matters was completely decomposed. The lignin- char produced could have also influenced the radical degradation mechanism of the plastics, hence an increased temperature in the thermal degradability of the plastics occurred. All these combined might have caused the experimental plastic maximum decomposition temperature peak less than the absolute value of simulation. These phenomena are in good agreement with those reports published by(Jakab, et al.,2001; Aboulkas, et al.,2008).

In Figure (3b), the bone-lignin mixed pyrolysis process shows that TG and DTG curves of simulation were basically consistent with the experimental curve. Since the bone material is a residue after composting, fatty substances contained in bone has undergone biological decomposition during the composting process. Inorganic substances such as calcium carbonate decomposed at 720^{o}C. This peak was also conspicuous in lignin matters, but with relatively low peak intensity when compared to bone residues. The bone–lignin residues from bio-treated food waste displayed similar thermal conversion characteristics, but with different decomposition peak intensities.

In Fig (3c), calculated value of plastic weight loss peak temperature was greater than the absolute value of the experiment. Whereas the bone residues show consistency with the calculated and experimental value in the range of 335^{o}C – 380^{o}C before decomposition variation occurred. This phenomenon was equally observed with the lignin-plastics mixtures. During the co-pyrolysis of the two samples, heat and mass transfer might have been slowed down. It resulted to slow softening of plastics and further reaction with either the bone/lignin residues in the solid phase pyrolysis. However, in Fig.3d, it shows calculated and experimental TG and DTG curves for complete mixtures of the three components from bio-treated food waste. Synergistic interactions were not observed among residues at lower temperature, only similar pyrolysis trend was displayed by lignin and bone residues. Meanwhile, noticeable interaction was observed at the solid phase of pyrolysis where lignin and bone char residues were further decomposed along the plastic phase. It was commented that the mechanism of the synergistic effect between biomass and plastic during co-pyrolysis is unclear (Zhou et al., 2015). It further explains why calculated and experimental curve for plastics decomposition peak at 500^{o}C does not overlaid.

3.3 Pyrolysis kinetics analysis

Generally, the kinetics of thermal decomposition reactions of biomass materials and plastics has very complex nature Their decomposition involves a large number of reactions both in parallel and in series. However, thermo-gravimetric analysis will provide general information on the overall reaction kinetics, rather than an individual reaction. This could be used as a tool for providing comparison of kinetic data of various reaction parameters.

The pre-exponential factors and activation energies of all the three residues in single and mixed proportions are presented in Table 2. Kinetic mechanism for the three materials in different stages of decomposition for single activation energies are between 22-62E(kJ/mol). These activation energies are small, hence, the three materials showed suitability for pyrolysis reaction. Lignin and bone substances as single components of second order reaction, displayed some complex characteristics at high temperature range.

Table 2: kinetics parameters for single and mixed residues

Samples	Temperature(^{o}C)	Y=aX+b	n	R^2	E(kJ mol^{-1})	A(min^{-1})
Experimental						
Lignin	220-350	y = -3703.4x - 7.1168	1	0.9715	30.79	30.05
	350-420	y = -7524.5x + 0.2083	3	0.9983	62.56	92670.43
Bone	220-350	y = -2726.7x - 8.9855	1	0.9669	22.67	3.41
	350-420	y = -5921.1x - 2.9817	3	0.9933	49.23	3002.39
Plastic	310-360	y = -5001.9x - 5.6388	3	0.9851	41.59	177.92
	360-510	y = -5588.8x - 5.4861	1	0.8507	46.47	231.60
LP - 8:2	230-360	y = -4005.2x - 6.7482	1	0.9879	33.30	46.98
	360-430	y = -6221.8x - 2.2625	3	0.9985	51.73	6476.27
	430-510	y = -8623.2x + 0.0773	2	0.9641	71.69	93162.13
LB- 8:2	220-350	y = -3534.9x - 7.4572	1	0.9774	29.39	20.41
	350-400	y = -5353.3x - 3.692	2.5	0.9996	44.51	1334.16
BP-6:4	310-360	y = -6428.5x - 2.5287	3	0.9967	53.45	5127.54
	450-510	y = -13741x + 7.0148	3	0.9856	114.24	1.53E+08
LBP-69:18:12	200-360	y = -3088.2x - 8.2097	1	0.9651	25.68	8.40
	360-410	y = -5848x - 2.6714	3	0.9978	48.62	4044.20
	410-510	y = -5038.7x - 3.9106	3	0.9953	41.89	1009.18
Calculated						
LP-8:2	230-360	y = -3849x - 7.0329	1	0.9854	32.00	33.96
	360-430	y = -5377.6x - 3.6732	3	0.9989	44.71	1365.65
	430-510	y = -14212x + 8.6674	3	0.971	118.16	8.26E+08
LB-8:2	220-350	y = -3547.8x - 7.4143	1	0.971	29.50	21.38
	350-400	y = -3240x - 7.5565	1.5	0.9994	26.94	16.94
BP-6:4	310-360	y = -5762.1x - 3.8363	3	0.9951	47.91	1243.07
	450-510	y = -21300x + 17.3	3	0.9706	177.09	6.95E+12

LBP-69:18:12	200-360	$y = -3220.3x - 8.0759$	1	0.9643	26.77	10.01
	360-410	$y = -6036.9x - 2.5608$	3	0.9992	50.19	4663.08
	410-510	$y = -9370.7x + 2.1241$	3	0.97	77.91	783893.3

N/B- LP: lignin mixed with plastic; LB: lignin mixed with bone; BP: bone mixed with plastic; LBP: lignin –bone –plastic mixed together.

Meanwhile, plastic had higher activation energy at high temperature range of 360-500°C, but lower activation energy in the first order reaction. The kinetics mechanism of the three residues activation energy exhibited no irregularity process compared to single components. In the mixture of lignin and plastic at a temperature corresponding to the 2nd stage, the activation energy is substantially greater than the activation energy of a single material which indicates that mixing the two residual matters. Solid parts of the decomposition process exhibit some inhibition which was consistent with the foregoing analysis. The decomposition temperature ranges during process of pyrolysis initially evolve gaseous escape from lignin. Subsequently, lignin - char residues decomposition with plastic might to certain extent influenced high activation energy at this stage. The respective changes of activation energies of mixtures showed that plastic and lignin residues of various compositions have different pyrolysis reactivity's at the respective temperatures. Wu, et al., (2015) reported kinetics and behavior of co-pyrolysis of algae residues and polypropylene synergistic effect achievable at mixture ratio of 6:4.

The mixture of lignin and bone at low-temperature range in the first phase exhibit low activation energy. While in the second phase of high-temperature range, the activation energy increased a little, unlike lignin residues pyrolysis alone, it has higher activation energy demand. In the high-temperature range, 2nd stage of lignin-bone pyrolysis, maybe, inorganic substances of bone that mixed with lignin decomposition has played a catalytic role.

The activation energy for mixture of bone and plastic is greater than the activation energy of a single material. The activation energy increases because plastic decomposition was inhibited with pyrolytic carbon-based material from bone pyrolysis decomposition, compared with single plastic decomposition pyrolyzed alone. The bone-char residues in the pyrolysis stages slowed down the reaction process and causing long reaction process. Hence, it was observed that activation energy increased almost double in the second phase of pyrolysis. It was reported that reactions with high activation energy requires a high temperature or a long reaction time (Lazaro et al., 1998).

Considering mixture of three materials (lignin, bone and plastic), the corresponding temperature range has lower activation energy than the activation energy of a single material. Perhaps, it might be due to the lower proportions of bone and the plastic material. Inhibition effect of carbon-based residues was not prominent, while catalytic role in the pyrolysis reaction promotes decreased activation energy. Therefore, the ratio of the residues LPB-69:18:12 after bio-treated food waste exhibit certain synergy in the pyrolysis process. At a lower temperature less than 350°C, activation energies of the experiment and simulation of mixed materials of L-B, L-P and B-P, shows low interactions. In comparison to the three mixtures, it might be due to low temperature catalytic synergy of different materials. Kinetic phenomenon among the three mixtures shows no inhibition of residual chars on plastic pyrolysis, a reduced reaction rate was equally displayed. Hence, at temperature (>350°C) the activation energy was lower than the experimental and simulated activation energy of B-P and L-P. This implied that bone matters and lignin materials pyrolyzed together with plastic enhanced cracking. At the same time, inorganic substances of calcium and silicon from bone exhibit certain catalytic performance. This speed up the reaction rate, resulting in decreased activation energy. Therefore, the three collective residues from bio-treated food waste, when subjected to temperature above 350°C, exhibited synergistic pyrolysis behavior, evidenced by the low activation energy trend.

4. Conclusions

(1) The characterization of bio-treated food waste comprised of lignin residues, bone, plastic and others in percentage fraction of 69%, 18%, 12%, and 1% respectively.

(2) Thermal decomposition of lignin and bone biomass maximum temperature peak is lower, weight loss temperature occurred at 335℃ in both materials. Plastic matters decomposition maximum peak occurred at high temperature of 476℃, whereas, it substantially decomposed completely at 500℃ when mixed.

(3) It was observed that in the three different residues combinations, the experimental TG/DTG curves and calculated TG/DTG curves were in good agreement. However, in the part of the different components of the solid phase pyrolysis process, no substantial agreement was noticed.

(4) In the combination of three different matters, it shows that at low-temperature pyrolysis stage (<350 ℃), no synergy was exhibited between different combinations. Meanwhile, in the high-temperature phase (> 350 ℃), catalytic effect from bone shells inorganic substance might have influenced the low activation energy observed. Furthermore, no inhibition of carbon-based residues from bone and lignin on plastic decomposition was noticed.

(5) The overall mixing ratio of the three residues from bio-treated food waste has displayed properties promoting their appropriateness for disposal through pyrolysis process.

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Conflict of interest The authors declare that there is no conflict of interest.

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