Energetic valorization of MSW compost valorization by selecting the maturity conditions.

by

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Abstract

MSW compost valorization under combustion, at two different composting process conditions, have been studied by thermogravimetric analysis (TGA). The composting operating parameters such as aeration and moisture affect the biodegradability of compost and results of the combustion (different gross heating values for each reactors). The obtained TGA showed that maximum weight loss for 10-12 % (245-247 ºC), 32-34 % (407-411 ºC) and 44-46 % (760-769 ºC) in correspondence to hemicellulose, cellulose and lignin-humic-fulvic acids decomposition for each reactor are observed. Obtained valued in kinetic study (Flynn-Wall-Ozawa method) results in suitable coefficients of determination. In that form, to establish the assumption that combustion of compost under a first-

order reaction may be appropriate. Moreover, in both reactors, the conversion rate increased and the activation energy decreased with composting time is found. The maximum gross heating value versus minimum activation energy (for α=0.25 and α=0.5) corresponds to final composts and under aeration of 0.050 and 0.175 L_{air} kg^{-1} d^{-1} and moisture of 40 % and 55 % for R1 and R2 reactors respectively. For MSW, under proper conditions, composting could be used as a suitable biodrying process, stabilizing and concentrating the heating value.

Keywords

MSW, combustion, compost, kinetic, TGA.

1. Introduction

In recent years, the better life standards of population around the world in general and in Europe specifically, has led a bigger use of goods and energy. It is therefore for a higher generation of Municipal Solid Waste (MSW) than ever (Aracil et al., 2017). The consumption has become in this way as consumers can choose between more options. This is why products usually take less time and only they can be used one time.

The average quantity of MSW produced, in the European Union has grown in the last years (Cabeza et al., 2013a) and to reduce the environmental impact, the European Commission has a new goal for 2030. Getting least 65 % recycling and reusing municipal waste (Malinauskaite et al., 2017). To overcome these objectives, effective management methods for wastes should be created (Moh and Abd Manaf, 2017). According to Zhang and Sun (2014), traditional practices

such as waste incineration or landfill are unwelcome. Firstly, landfilling is the most used MSW disposal method. However this option is not considered sustainable, due to occupying land and for the risk of leaching of contaminant from MSW incineration bottom ash, for example heavy metals and soluble salts (Verbinnen et al., 2015)

Another widely used way to remove the amount of MSW is the incineration, especially in regions with land-space problems and high number of unhabitants (Stehlík, 2009). However, this process generate MSW incineration bottom ash and fly ash; the last having leachable heavy metals, chlorides, and organic contaminants (Erol et al., 2007; Li et al., 2018).

Thus MSW incineration bottom ash represents aproximadately 90 % of the residue by mass, around 10 % by volumen (Stegemann et al., 1995) and they have been considered for its engineering applications but still exist potential enviromental risks as its high porosity and alkali-silica reaction (Xuan et al., 2018).

In this sense, the European Commission reported that only a 43 % of the generated municipal waste is recycled, 31% landfilled or directly incinerated (26 %) (Malinauskaite et al., 2017). In terms of the MSW´s role plays in the green economy, the European Union request a strategy of prevention and recycling or composting.

Composting has awaked a greater interest in the use and disposal of organic waste in a way that respect the environmental (López et al., 2016). In addition, composting drive the translation of waste into value-added products (Qian et al., 2014). Composting is known as a biological decomposition and

stabilization process of organic matter, under conditions that provide the development of thermophilic temperatures as a result of biologically generated heat, to produce a final product that is stable, free of pathogens and plant seed and can be beneficially applied to land (Haug, 1993).

Composting has some advantages compared with other uses from MSW. Nowadays, a challenge for researches is the optimization of composting processes (Cabeza et al., 2013b). It is a useful tool for managing ad recycling large quantities of MSW (Raut et al., 2008). Also, composting contributes to the reduction of persistent organic compounds (Li et al., 2015). It has been shown that the use of compost generates better results in the agricultural sector than artificial fertilizers (Chowdhury et al., 2015). According to Hermann et al. (2011) composts plays a key role in the formation of humus, which cannot be achieved in another way. The humic-like fraction of compost push plant growth and prevents the appearance of phytopathogens (Traversa et al., 2010). In conclusion, this treatment is in total agreement with sustainable agriculture (Muscolo et al., 2018).

Nevertheless, the only way to produce a quality compost is to carry out on adequate management of the composting process (Storino et al., 2016; Zhang and Sun, 2016). Composting may have negative effects on the soil, such as the increase in the risk of phytotoxicity or a higher concentrations of toxic elements (Jordão et al., 2003). The cumulative effects of composting on the soil should be investigated in the future (Fagnano et al., 2011).

Due to environmental problems, marketing, overproduction, rising level of stocks marketing, etc., some quantities of produced compost cannot be used for its main purpose.

A possible alternative to valorize this product could be compost combustion to obtain energy. In this sense, few bibliographical references regarding MSW compost incineration have been found. Therefore, the objective of this paper is to measure the evolution (compost age) and influence of the type of composting on the real product heat capacity, as well as its activation energy in the combustion process and get the most profitable operating conditions have to obtain a product easily incinerable. In the present study, the obtained activation energy (Ea) values could be used to determine composting optimum conditions and maturity for maximum energy efficiency (calorific value) with the minimum Ea value.

2. Materials and methods

2.1. Raw material and composting

Municipal Solid Waste come from Villarrasa's (Huelva-Spain), from an urban waste treatment plant. This waste is selected for composting. The first step prior to composting is the magnetic separation of ferrous metals and non-ferrous metal materials using a bag-opener trommel. Some relevant characteristics of MSW are given in Table 1.

Property	Units	MSW[b]	Compost Reactor 1 (after 40 days)	Compost Reactor 2 (after 40 days)
pH (1:5 extract)		5.9 ± 0.2	6.9 ± 0.1	7.0 ± 0.1
EC (1:5 extract)	ds m^{-1}	8.3 ± 0.7	10.2 ± 1.3	11.1 ± 0.9
Organic Matter[c]	g kg^{-1}	702.0 ± 28.9	598.0 ± 31.6	573.0 ± 27.5
Kjeldahl-N	g kg^{-1}	22.1 ± 0.8	13.0 ± 1.3	17.4 ± 1.5
C/N		19.1	24.3	20.0
Particle size				

>25 mm	%	55.2 ± 8.9
25-10 mm	%	27.3 ± 5.4
10-5 mm	%	9.9 ± 2.8
5-2 mm	%	4.9 ± 1.6
<2 mm	%	2.7 ± 1.0

[a] Average ± standard derivation.
[b] MSW: Municipal solid waste.
[c] Determined in MSW <5 mm and free of impurities.

Table 1. Relevant characteristics of municipal solid waste (over dry basis) used in this study (average ± standard deviation[a]).

Two different composting processes (under different parameters) have been studied (Table 2). The volume of composting reactors were of 200 L. To reduce the conductive heat loss, the reactor surface area was covered with polyurethane foam. Compressed air (at different rates for each reactor) was entered in the reactor and dispersed by perforated plate. To keep initial conditions and to produce significant environmental differences between both composting processes, water loss was compensated by the addition of water during active composting. In Table 2 the composting characteristics for both reactors (R1 and R2) are shown. Two levels of moisture levels had been fixed (40 and 55 % for R1 and R2 respectively) before the experimental procedure to obtain a stable product during composting. Each one was half filled with 40 kg of MSW. Two samples of approximately 100 g were taken from, at least, 2 locations next to the reactor and from different depths at each day.

Reactor	Aeration (L kg^{-1} d^{-1})	Moisture (%)
1	0.050 ± 0.003	40 ± 2

2	0.175 ± 0.009	55 ± 3

Table 2. Composting Characteristics.

After of the composting process, an elemental analysis was carried out for the obtained samples. This material used, was analyzed for the following elements: nitrogen, carbon, hydrogen and oxygen. The chemical characterization of raw material and obtained compost used in this study are shown in Table 3.

	Sample	Carbon	Oxygen	Hydrogen	Nitrogen	P_2O_5	K_2O	Mg	Na	Fe
R1	Day 1	29.4 ± 0.9	12.7 ± 0.5	3.9 ± 0.2	4.8 ± 0.3	0.7 ± 0.02	0.6 ± 0.5	3.3 ± 0.1	0.5 ± 0.2	0.6 ± 0.2
	Day 10	26.4 ± 1.2	13.3 ± 0.6	2.4 ± 0.2	3.9 ± 0.2	0.8 ± 0.03	0.7 ± 0.6	3.3 ± 0.1	0.6 ± 0.2	0.7 ± 0.2
	Day 20	23.1 ± 1.1	13.0 ± 0.6	3.3 ± 0.2	4.1 ± 0.2	0.8 ± 0.02	0.7 ± 0.6	4.5 ± 0.2	0.6 ± 0.2	0.7 ± 0.2
	Day 40	19.0 ± 0.7	12.6 ± 0.6	3.1 ± 0.2	4.2 ± 0.3	0.7 ± 0.03	0.6 ± 0.6	3.8 ± 0.1	0.5 ± 0.2	0.9 ± 0.3
R2	Day 1	29.3 ± 1.1	12.7 ± 0.6	3.8 ± 0.2	4.9 ± 0.2	0.8 ± 0.03	1.1 ± 0.05	3.2 ± 0.1	1.0 ± 0.4	0.5 ± 0.2
	Day 10	26.1 ± 1.4	11.3 ± 0.6	2.8 ± 0.2	4.6 ± 0.3	0.7 ± 0.02	0.9 ± 0.05	4.4 ± 0.2	0.7 ± 0.3	0.4 ± 0.2
	Day 20	24.7 ± 1.2	16.4 ± 0.8	2.6 ± 0.2	3.7 ± 0.2	0.7 ± 0.03	0.8 ± 0.04	4.8 ± 0.2	0.7 ± 0.3	0.4 ± 0.2
	Day 40	21.5 ± 1.0	13.8 ± 0.6	3.5 ± 0.2	4.0 ± 0.3	0.8 ± 0.03	1.1 ± 0.05	5.2 ± 0.2	0.8 ± 0.3	0.5 ± 0.2

Table 3: Chemical characterization of R1 and R2 compost (%).

2.2. Analytical Methods

Raw material from MSW samples were collected before the beginning of the experiment. In MSW particle size distribution was determined by a sieve shaker, and other materials as glass, plastics, metals and stones were hand separated and weighed. After combustion at 540 ºC, total organic matter was determined by the weight loss, and organic carbon was calculated multiplying organic matter by 0.58 (Haug, 1993). Nitrogen was determined by steam distillation after Kjeldahl digestion. Organic matter and nitrogen determinations were done in the <5 mm size fraction. Moisture in compost samples was determined by the water fraction loss in the heater. The pH was determined in a 1:5 (in weight) compost: water extract using a pH electrode.

The Gross Heating Values (constant volume) were calculated in line with "CEN/TS 14918:2005 (E) Solid biofuels-Method for the determination of calorific value" and "UNE 164001 EX standards" using a Parr 6300 Automatic Isoperibol Calorimeter.

Biodegradability (Kb) (Diaz et al., 2002) was calculated for each mixture using the Equation 1.

$$K_b = \frac{\left[\left(OM_i - OM_f\right)\cdot 100\right]}{\left[OM_i\left(100 - OM_f\right)\right]} \qquad \text{Eq. (1)}$$

where:

OM_f is the organic matter content when the process finish and

OM_i is the organic matter content at first of the process.

2.3. TGA and kinetic modelling

Thermo-chemical combustion behavior was explained using a thermo-gravimetric analyzer (Mettler Toledo TGA/DSC1 STARe System). The thermal

gravimetric analysis (TGA) experiments were done by heating a 100-130 mg sample from 25ºC to 800ºC under four heating rates of 5, 10, 15 and 20ºC min^{-1} under a nitrogen and oxygen flow of 15 and 10 mL min^{-1} respectively.

Kinetic parameters estimation based on TGA data could be performed by different techniques known as model-fitting and model-free including kinetic reaction model identification or not. In the first type, kinetic parameters are calculated by assuming the form of degradation equation and it is difficult to get data in an appropriate way. So that is why the model-fitting methods could produce unknown values of kinetic parameters (Radojevic et al., 2018). The model-free methods (e.g., isoconversional, etc.) could be considered as single-step kinetics. On the basis of the foregoing, the use of the isoconversional methods has been recommended to the combustion kinetics determination. Beyond these isoconversional estimations, the integral method of Flynn-Wall-Ozawa could be the most commonly used (Vyazovkin et al., 2011).

Kinetic analysis by Flynn-Wall-Ozawa (FWO) method activation energy describes the reaction modifications as a function of temperature. For a single-reaction method, activation energy should be a constant value for each weight loss region. The activation energy values determined by FWO method (Flynn and Wall, 1966; Ozawa, 1965) is defined by Equation 2.

$$\ln(\beta) = \ln\left(\frac{AEa}{Rg(\alpha)}\right) - 2.315 - 0.4567\frac{Ea}{RT} \qquad \text{Eq. (2)}$$

In this equation, β is the heating rate, A is the pre-exponential factor, g is a function of the conversion, Ea is the activation energy, T is the temperature and R is the gas constant. A linear relationship can be accomplished a given degree of conversion (α) and for different heating rates by plotting the heating rates logarithm (ln β) versus (1/T).

Diverse temperatures have been achieved from different TGA thermal curves at several heating rates resulting a slope (0.4567 (Ea/R)) from which the activation energy could be obtained. The conversion degree points used for the estimation of Activation Energy have been selected according to the maximums obtained in the differential mass loss thermograms. The conclusion is that the reaction mode is identical to a certain degree of conversion (α) in reactions under different conditions.

3. Results and discussion

3.1. Composting process

The variation in composting conditions caused different temperature profiles among composting process (data non shown). However, the three typical phases of composting were observed: (i) a short initial mesophilic phase (T<40 ºC) lasting approximately 2 days, (ii) a thermophilic phase, during which the temperature increased (T>40 ºC) 5 days for both reactors, during this phase, R1, and R2 reached a maximum temperature of 55 and 58 ºC at 6 and 8 days of composting respectively, (iii) a maturation phase, when the temperature decreased slowly to mesophilic values above 40 ºC in the mixtures. In this sense, the mesophilic profile for both reactors were similar. At the end of the experiment after 40 days of composting the temperature remained at ambient temperature in both reactors.

Organic matter content decreased during composting for all mixtures (Table 1). Differences in process conditions, apart from observed differences in the temperature profile, affects the amount of organic matter degraded and significant differences have been found. In this sense, lower values of biodegradability (K_b=0.36) for R1 and higher values (K_b=0.42) for R2 have been

calculated. Consequently, the higher biodegradability values were obtained under R1 composting conditions.

3.2. Heating value evolution under composting process

Different gross heating values (dry basis) evolution for both reactors are observed (Figure 1).

The gross heating values was decreased with increase in time interval of composting process for both reactors. This could be because ash increment (due to the organic matter, with high calorific value, mineralization) during the most active phases of the composting process. High ash content can decrease the heating value of biomass (Senelwa and Sims, 1999).

It was reported by Komilis et al. (2014) that heating values must be lower at the end of active composting process. The low value of gross heating values indicates small amount of energy produced under combustion at the end of the composting active phase.

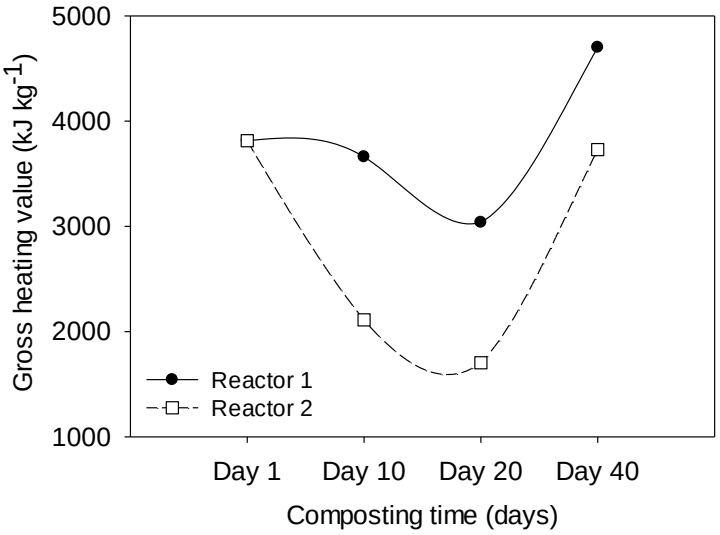

Fig.1: Heating value evolution (dry basis) under composting process for R1 and R2.

The Figure 1 shows the comparison of heating values for R1 and R2. In this sense, the process conditions affect the value of the obtained results. Low composting degradation (higher organic matter content) shows higher heating values (3038.07 and 1703.76 kJ kg^{-1} for R1 and R2 respectively). After the maturation stage (40 days), a clear increase (in both reactors studied) has been observed (4701.84 and 3725.36 kJ kg^{-1} for R1 and R2 respectively). The increment could be due to fulvic and humic formation during this composting phase. According to Kastanaki et al. (2002) the humic and fulvic acids heating values are comparable to that of pure lignite (coal).

3.3. Thermogravimetric analysis of the combustion process

The effect of the heating rate on thermal degradation (TGA) and differential mass loss (DTG) thermograms of compost from two reactors (R1 and R2), at four dates (day 1, 10, 20, 40), under 15 ºC min^{-1} heating rate, are analyzed (Figures 2 and 3).

As expected, the four typical regions on TGA and DTGs are evident which correspond to water evaporation, hemicellulose, cellulose, lignine and humics and fulvics acids degradation in the figures are found.

Thermal oxidation analysis of the compost shows some several peaks. For both reactors, first region from 60 ºC to 120 ºC is related to the extraction of moisture and adsorbed water in samples, also two higher peaks between 200 and 450 °C (related to hemicellulose and cellulose decomposition) (Gunasee et al., 2016) are observed. The decomposition process depends on the composition and concentration of its main biomass components (cellulose, hemicellulose and lignin). In that form, the decomposition of hemicelluloses and cellulose take place in the temperature from 200-300 ºC and 400-450 ºC, respectively.

In the TGA thermograms for Reactor 1 are showed the maximum weight loss for 15 %, 34 % and 44 %. Furthermore, in The DTG thermograms, greatest degrade hemicellulose, cellulose and lignin-humic-fulvic acids decomposition are found at 247 ºC, 411 ºC and 760 ºC respectively (Figure 2). The higher activity of hemicellulose in thermal decomposition might be attributed to its chemical structure. Hemicellulose has a chaotic structure and it is easily hydrolyzed (John and Thomas, 2008; Yang et al., 2006). In contrast, the cellulose has a long polymer´s chain of glucose units, which contains crystalline regions that improve thermal stability for materials (Yang et al., 2006).

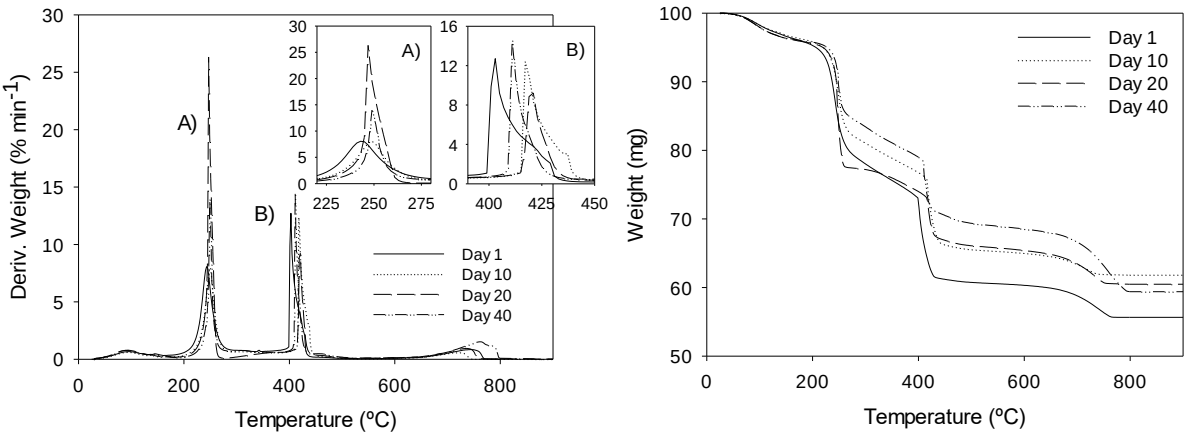

Fig. 2: DTG and TGA curves of the samples collected at different times of the composting process in Reactor 1.

For the Reactor 2 the highest weight loss for 12 %, 32 % and 46 % are showed in the TGA thermograms and the decomposition of the previous components are found in the DTG thermograms to 245 ºC, 407 ºC and 769 ºC (Figure 3). For both reactors, biggest peak of hemicellulose decomposition was attributed to 40-day of composting process and for cellulose decomposition to first-day.

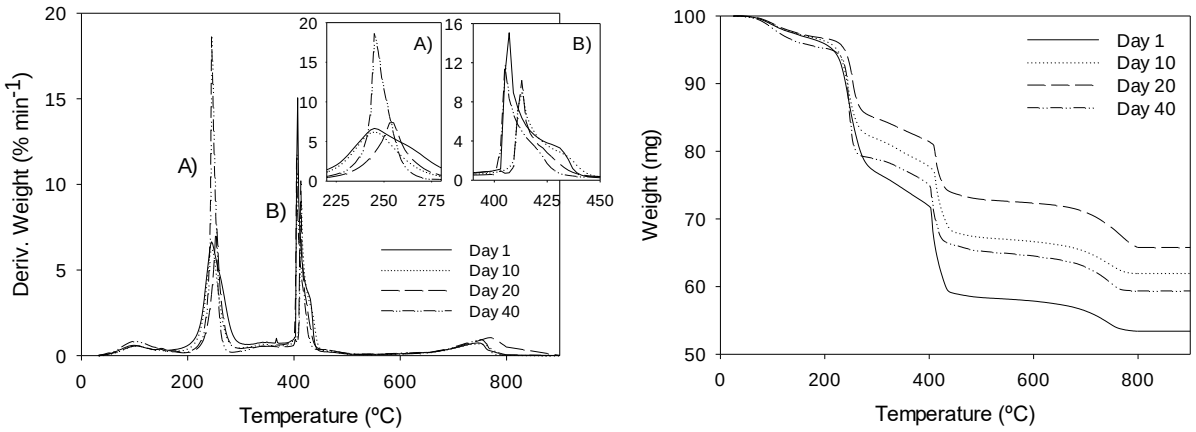

Fig. 3: DTG and TGA curves of the samples collected at different times of the composting process in Reactor 2.

For both reactors, lignin is decomposed in both stages (Dantas et al., 2013) in range during all the decomposition´s process without characteristic peaks. Residual cellulose is protected by lignin after the temperature reaches 350ºC (Gunasee et al., 2016; Loaiza et al., 2017). Lignin is composed of three kinds of benzene-propane units, being heavily cross-linked and contain very high molecular weight (John and Thomas, 2008; Yang et al., 2006). For this reason it has a very high thermal stability and his decomposition is complicated (Yang et al., 2006).

As the composting process advanced, the intensity of the second peak increased, while the first one slightly decreased. The presence, in the final composts (in both reactors) of a more intense peak in the 750-800 ºC shows a distinctive character of humified organic matter (Wu et al., 2011; Zahra El Ouaqoudi et al., 2015) This fact could be related to an increase of molecular weight, stability, and aromatization degree during the composting process (Pietro and Paola, 2004).

Despite differences in aeration and moisture between both reactors (Table 2), significative differences are not found neither temperature peaks nor for maximum weight loss rate.

3.4. Kinetic analysis

The activation energy (Ea) for the raw material and the obtained composts have been obtained using FWO method. The variation of activation energy as a function of the composting conditions and time, calculated using Eq. (2) was presented in Table 4. The FWO equations of ln(β) versus 1000/T for two different values of conversion are shown in this table. The activation energies were derived from the slope. The regression coefficients and the square of the correlation coefficient (R2) is also presented. In that table, could be seen that all the regression results in suitable coefficients of determination, R^2 (from 0.94 to 0.99). In that form, to establish the assumption that combustion of compost under a first-order reaction may be appropriate. The activation energy in final composts (day 40), both for α=0.25 and α=0.5, have been higher than that for initial (day 1), thermophilic (day 10) and medium composting process (day 20).

Conversion degree		α=0.25				α=0.5			
	Sample	a	b	R^2	Ea (KJ mol^{-1})	a	b	R^2	Ea (KJ mol^{-1})
R1	Day 1	-47.67	90.11	0.99	239.22	-17.46	28.81	0.99	101.48
	Day 10	-46.84	65.86	0.99	225.43	-13.11	17.71	0.99	82.58
	Day 20	-45.20	87.89	0.94	228.24	-12.24	18.94	0.94	60.11
	Day 40	-41.35	78.27	0.96	108.96	-11.76	8.366	0.99	55.97
R2	Day 1	-66.03	98.70	0.98	266.65	-21.56	32.44	0.99	109.67
	Day 10	-51.46	83.23	0.97	236.43	-19.08	29.53	0.98	89.14

Day 20	-46.13	87.62	0.99	215.62	-18.01	27.31	0.95	81.55
Day 40	-37.21	54.57	0.99	159.79	-13.13	20.57	0.94	70.20

Table 4: Arrhenius activation energy evolution for both reactors under two conversion degree (α).

The activation energy was not similar for all conversion indicates the existence of a complex mechanism that occurs in the solid state. From Table 4, similar to that found in Figures 2 and 3, it can be seen that compost combustion shows typical characteristics for multi-step reaction and main decomposition occurred at the conversion from about 25 % to 50 % (α=0.25-0.5).

In the first-step reaction (α=0.25), It is higher at the beginning of the process because it has greater amount of hemicellulose with an activation energy higher than other biomass components (Rakthong et al., 2015).

Activation energies for α=0.5 are generally lower than for α=0.25. This may be because, in this phase, it is the degradation of the cellulose components that marks the value of its activation energy. The variation trend was similar to that found for the first-step reaction. When the conversion increased above 50 %, the activation energy declined rapidly, which probably attributed to greater presence of ash in the solid residue (Álvarez et al., 2016).

Leroy et al. (2010) showed that the activation energy decreased 125 to 40 kJ mol^{-1} with increasing combustion conversion.

3.5. Compost combustion optimization

Figure 4 shows gross heating value vs activation energy for for α=0.25 and α=0.5 in both reactors.

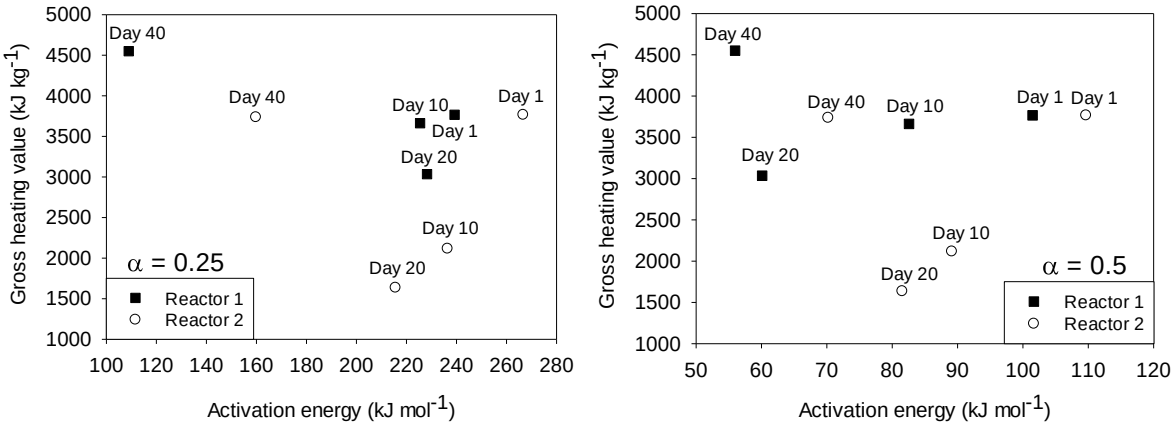

Fig. 4: Gross Heating Value evolution (kJ kg^{-1}) under activation energy (kJ mol^{-1}) for α=0.25 (a) and α=0.5 (b) for R1 and R2.

In both figures, maximum heating values for R1 (minimal degradation, aeration of 0.050 L_{air} kg^{-1} d^{-1} and moisture of 40 %) compost could be observed. Both, for α=0.25 and α=0.5, the maximum gross heating value for minimum activation energy corresponds to day 40 of composting under R1 conditions. Interestingly, under different conditions of composting (R2, aeration of 0.175 L_{air} kg^{-1} d^{-1} and moisture of 55 %) lower heating value and higher activation energy with respect to R1 conditions have been obtained.

4. Conclusions

Combustion behaviors of MSW compost under two different composting process conditions have been studied in TGA.

Different biodegradability values for R1 (K_b=0.36) and for R2 (K_b=0.42) have been calculated and distant gross heating values for both reactors are observed. Therefore, the process conditions affect the obtained heating.

In the obtained TGA for both Reactors showed the maximum weight loss for 10-12 % (245-247 ºC) 32-34 % (407-411 ºC) and 44-46 % (760-769 ºC) in

correspondence to hemicellulose, cellulose and lignin-humic-fulvic acids decomposition.

The activation energy (FWO method) in final composts, both for α=0.25 and α=0.5, have been higher than that calculated for initial, thermophilic and medium composting process. Moreover, higher gross heating value versus minimum activation energy ratio under aeration of 0.050 L_{air} kg^{-1} d^{-1} and moisture of 40 % with respect to aeration of 0.175 L_{air} kg^{-1} d^{-1} and moisture of 55 % is found.

For MSW, under R1 composting conditions (aeration of 0.050 L_{air} kg^{-1} d^{-1} and moisture of 40 %), could be used as a suitable boydrying process, stabilizing and concentrating the heating value.

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