Pyrolysis of Municipal Solid Waste compost: pilot plant evaluation as a sustainable practise of waste management.

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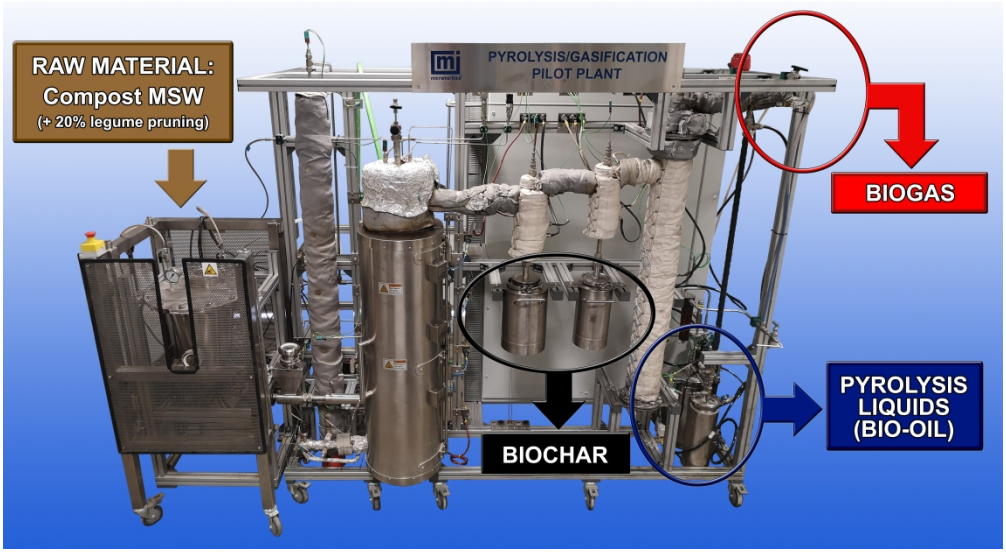

Graphical abstract

4406x2413mm (38 x 38 DPI)

Highlights

— MSW Compost pyrolysis in pilot plant has been evaluated.

— The process kinetic to the pyrolysis of lignocellulosic materials could be assimilated.

— Compost can produce a low stability biochar in soil with low aromaticity.

— Bio-oil produced is composed of a highly phenolic fraction.

— Biogas of pyrolysis compost is a mixture of short-chain organic compounds.

Pyrolysis of Municipal Solid Waste compost: pilot plant evaluation as a sustainable practise of waste management

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Abstract

To evaluate the potential of compost based on Municipal Solid Waste (MSW) and 20% legume pruning under a pyrolysis process, generated products, including solids (biochar), liquids (bio-oil) and gases (non-condensable gases), through experimentation in a pilot plant with a fluidised bed reactor at 450 °C and gas chromatography/mass spectrometry (GC/MS) have been analysed. Also, the compost kinetic behaviour by thermogravimetric analysis (TGA), using Flynn-Wall-Ozawa method, has been investigated. Four different reaction zones, associated with lignocellulosic materials (hemicellulose, cellulose and lignin) with a first step for water evaporation, in TGA curve have been observed. A biochar with low stability and aromaticity, considering high and low O/C and H/C ratios, respectively, has been obtained. The obtained pyrolytic liquids contain a high concentration of phenolic compounds because of a significant presence of lignins and other high molecular weight compounds in the original material. Moreover, the generated non-condensable gases consist mainly of short-chain compounds such as alcohols, aldehydes and alkenes produced from hemicellulose, cellulose and proteins.

Keywords: pyrolysis; MSW compost; kinetic; GC/MS; biochar.

1. Introduction

It has been widely recognised that inadequate treatment of organic waste can lead to significant environmental and health problems. In this respect, the beneficial properties of compost both as a suitable solution for the treatment and sanitation of organic waste and its subsequent use in agriculture (both technically and economically) have been extensively demonstrated (Rashid and Shahzad, 2021). Despite the problems that inadequate management, mainly due to the odours emitted (Delgado-Rodríguez et al., 2011) can cause.

The quality of the final compost will depend significantly on the nature and quality of the waste to be composted. However, the process parameters are also involved in the degradation to which the organic compounds are subjected during composting. Therefore, a high variability of quality in the produced compost can be ascertained, and quality standards for its use in agriculture must be applied (Hameed et al., 2021). However, in addition to the traditional uses of compost, new uses and organo-mineral formulations (Fachini et al., 2021) are being developed.

In the EU-28 (28 EU Member States) approximately 88 million tonnes/year of food are wasted. About 20% of the food produced represents this value. Because of various problems, including lack of segregated sorting and impurities, only 17% of this municipal waste can be properly composted and/or digested (EEA, 2020). Therefore, a high proportion of composted Municipal Solid Waste (MSW) is not of a quality suitable for direct use in agriculture.

Consequently, various ways of valorization of this compost of low agronomic quality, apart from the alternative uses that are already being used, such as the recovery of degraded areas (mines, quarries, landfills), forestry crops, etc.,

should be explored. Therefore, enhancing the valorisation pathways of these materials to improve the management of these wastes should be developed.

Thermochemical processes, due to the wide range of products (solid, liquid and gaseous) and/or energy generated, are an alternative to be considered for the valorisation of organic materials. Among these, combustion (with an excess of oxygen over that required according to stoichiometry), gasification (with a deficit of oxygen over that required according to stoichiometry) and pyrolysis (without oxygen) can be noted (Beis et al., 2002).

In this sense, pyrolytic processes as a source of new high value-added products from compost can be highlighted. During composting, organic compounds are generally degraded or directly mineralized, although a portion of the high molecular weight compounds present in the original material increase the degree of aromaticity in the resulting composted compounds. Also, an increase in the mass degradation above 600 °C as the composting time increases (Díaz et al., 2021) is produced. Thus, the composting process significantly alters the distribution of chemical compounds and may result in products that may not be produced during pyrolysis of other sources of organic compounds.

Among these innovative materials from compost by pyrolysis, Qian et al. (2007) and Finney et al. (2009) used compost, from livestock manure and mushroom industry residues, respectively, as raw material for the production of biochar. Also, the use of composts, in the pyrolysis process, as a potential feedstocks for bio-oil production has been studied by Garrido et al. (2012) and Giwa et al. (2018).

The general objective of this work is to study the products generated (biochar, pyrolytic liquids and volatile organic compounds) during the pyrolysis of MSW

compost with 20% pruning residues. Also, the kinetics of the reactions produced during the pyrolysis of these composts has been studied.

2. Materials and Methods

2.1. MSW composition

The different components of MSW can be classified into three main groups: fermentable (food waste), combustible (paper, cardboard, plastics, rubber, textiles, wood, etc.), and inert (metals, glass, etc.). The composition of MSW is highly variable and depends on factors such as the standard of living, lifestyle of the population, and the time of year. The composition of the MSW composted in this study is shown in Figure 1.

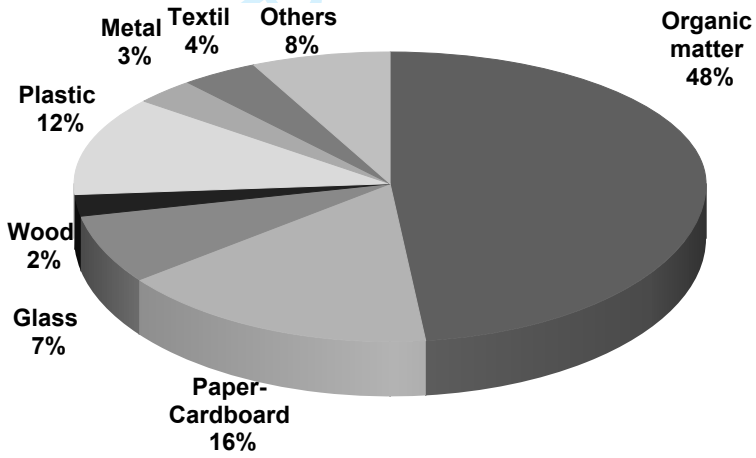

Figure 1. MSW composition.

2.2. Compost characteristics

Non-selective Municipal Solid Waste Compost (MSWC) from Villarrasa (Huelva - Spain) urban waste treatment plant is used in this study. Prior to composting the main treatment involves trammel-screening (8 cm), metal electromagnetic separation and manual separation of plastics. To improve internal aeration in composting piles, 20% of bulking material (legume pruning of *Leucaena*

leucocephala), before the composting process, have been added. The non-degraded fraction of this material was separated by screening at the end of the composting process. The most relevant chemical characteristics of the final compost are reported in Table 1.

Property	Units	Compost (after 40 days)
pH (1:5 extract)		7.8 ± 1.2
EC (1:5 extract)	dS m^{-1}	8.5 ± 1.1
Organic Matter	g kg^{-1}	593 ± 32
Kjeldahl-N	g kg^{-1}	12.3 ± 3.5
Ash	g kg^{-1}	35.4 ± 4.7
C/N		26.6
Moisture	%	0.6

[a] Determined in MSW <5 mm and free of impurities
[b] Mean values and standard deviations were calculated from the triplicates

Table 1. Relevant characteristics of used MSWC[a] (average ± standard deviation)[b]

2.3. Processing of the samples by pyrolysis with TGA

The dried compost samples, with an initial average diameter of 50 mm, were milled into particles of smaller size (1-2 mm). The final particles were stored without contact with air moisture. Thermochemical decomposition behavior was evaluated using a thermo-gravimetric analyzer (TGA) (Mettler Toledo TGA/DSC1 STARe System). TGA experiments heating 10-25 mg samples from 25 °C to 850 °C, at four heating rates (5, 10, 15 and 20 °C min^{-1}) under nitrogen flow rate of 20 cm^3 min^{-1} have been performed. The obtained thermo-gravimetric analysis data

for any changes in the thermo-chemical decomposition behavior have been studied.

2.4. Pilot plant pyrolysis

A laboratory-scale fluidized bed reactor (PID Eng&Tech Micromeritics) has been employed. An operating temperature of 450 °C has been used. 30 L min^{-1} of nitrogen (twice the minimum fluidization rate) has been used, with a constant pressure difference of 33 mbar.

A gas cleaning system at the reactor outlet has been installed. This system consists of two cyclones (CY1 for particles >20μm and CY2 for particles >5μm) that have been connected in series. Downstream, a heat exchanger (400ºC to 90ºC), controlled by a single valve, is used to regulate the inflow of the coolant fluid (water 20ºC) into the heat exchanger. Pyrolytic liquids in a cooling vessel (first condenser (CD1) at 63 °C), located at the bottom of the heat exchanger have been collected. Water and other condensed liquids are retained in a second condenser (CD2) (30ºC). Finally, the product gases pass through coalescing filters before sampling and finally into a scrubber (23ºC).

2.5. Pyrolytic liquid analysis

An aliquot to pyrolytic liquid has been extracted with water (1:10 ratio), vortexed 30 s and centrifugation for 20 min at 5000 rpm. Then, 1 mL the water-insoluble fraction was extracted with diethyl ether (DEE) (3 x 1 mL). After extraction, an aliquot DEE extract (500 μL) has been dried under nitrogen and 50 μL of both pyridine and BSTFA/TMCS (90:10) were added following incubated for 30 min at 60ºC. Then, TMS derivative extracts were diluted (1:10) with $CHCl_3$ and 1 μL was injected into GC-MS/MS (GCMSQP8030 Ultra System, Shimadzu, Japan). TMS derivative compounds were separated by a HP-5 MS column (60 m, 0.25 mm I.D.

0.25 µm film thickness, J&W Scientific, Agilent Technologies, USA). The GC oven was programmed: 50 °C for 2 min, ramped at 8 °C min^{-1} to 280 °C, held for 2 min. A second ramp rate was performed of 50 °C min^{-1} until a final temperature of 300 °C was reached and held for 2 min. Helium at constant flow rate of 1.20 mL min^{-1} was used as the carrier gas. The temperatures of the injection port (split mode 10:1), transfer line and ion source were maintained at 250, 280 and 230 °C, respectively. The mass spectrometer was operated in scan mode (50-800 m z^{-1}). TMS derivative compounds were identified by comparison of the mass spectra with those of the database of NIST11 library. For control and data analysis, GCMS Postrun Analysis Shimadzu was used. The MS was turned with perfluorotributylamine (PFTBA).

2.6. Biochar analysis

Gross Calorific Value (constant volume) following the standards "CEN/TS 14918:2005 (E) Solid Biofuels - Method for the determination of the calorific value" and UNE 164001 EX have been determined. Automatic Isoperibol Calorimeter Parr 6300 has been used. Total carbon, hydrogen and sulphur simultaneously in a ELTRA Carbon/Hydrogen/Sulfur Analyzer CHS-580A (ELTRA GmbH, Germany) have been determined. The standard guidelines for the determination of carbon, hydrogen (EN 15104:2011) and sulfur (EN 15289:2011) have been followed. Moreover, oxygen content by difference (CEN/TS 14961, 2005) has been also calculated. According to ISO 10390:2005, biochar was air-dried and crushed into fine particles (<2 mm). Then, the sample was soaked with 0.01 M $CaCl_2$ at a 1:5 solid/water ratio for 1 h with agitation.

After still standing for 1 h, the slurry was then measured for pH using a pH-meter GLP 21 (Crison Instruments, S.A.).

2.7. Volatile compounds gas samples analysis by pyrolysis TD/GC-MS

Volatile compounds gas samples from the pilot plant pyrolysis process at 350 and 550ºC (corresponding to higher temperatures than the degradation maxima found in the TGA curves) were collected in fritted glass TD tubes (Supelco, Bellefonte, PA; O.D.: 6.35 mm; length: 88.9 mm) for 1.5 min. Tubes containing 100 mg of Tenax® TA (80-100 mesh purchased from Supelco, Bellefonte, PA) packed in layers of silanized glass wool. TD tubes after sampling have been analyzed using TD/GC-MS. TD was used to release the captured volatile compounds from the tube sorbent material onto the GC/MS for identification and quantification. TD was carried out by use of thermal desorption system unit (TD-20, Shimadzu, Japan) fitted with a HP-5 MS column (60 m, 0.25 mm I.D. 0.25 µm film thickness, J&W Scientific, Agilent Technologies, USA) and involved 2 steps: tube desorption and trap desorption. The mass spectrometer was operated in scan mode (41-450 m z^{-1}). Volatile organic compounds were identified by comparison of the mass spectra with those of in the database of NIST11 library using as internal standard 1-bromo-3-chlorobenzene (BCB). For control and data analysis, the GCMS Postrun Analysis Shimadzu was used. The MS was turned with perfluorotributylamine (PFTBA).

2.8. Kinetic analysis by Flynn-Wall-Ozawa method

The activation energy of pyrolysis reactions in lignocellulosic materials has been studied by several different mathematical methods. In this regard, the use of isoconversional methods for the determination of pyrolysis kinetics has been successfully documented (Açıkalın and Gözke, 2021). Moreover, according to the

results obtained by Fernández-López et al. (2016) and Palma et al. (2020), this model has been satisfactorily tested in different composts. Moreover, Gunasee et al. (2016) have demonstrated that this TGA-based experimental methodology could be suitable for revealing synergistic reactions during co-pyrolysis of different MSW.

For a given reaction, the activation energy should be a constant value throughout the weight loss region, so changes in these values imply degradation of other compounds. In the present study the activation energy values for the degradation process using the Flynn-Wall-Ozawa (FWO) isoconversional method (Flynn and Wall, 1966; Ozawa, 1965) defined by Eq. 1 have been determined. This method for determination of the Ea values without any knowledge of its mechanisms (El-Sayed and Mostafa, 2015) can be used.

$$ln\,(\beta) = ln(\frac{A\,Ea}{R\,g(\alpha)}) - 2.315 - 0.4567\,\frac{Ea}{R\,T} \quad \text{(Eq. 1)}$$

where β is the heating rate, A is the pre-exponential factor, g(α) is a function of the conversion, E_a is the activation energy and R is the gas constant.

Therefore, for different heating rates (β) and a given degree of conversion (α), a linear relationship is observed by plotting of natural logarithm of heating rates (ln β), versus (1/T) obtained from thermal curves recorded at different heating rates will be a straight line whose slope (–0.4567 (E_a/RT)) will calculate the activation energy.

3. Result and Discussion

3.1. Compost TGA analysis

Thermograms of compost (TGA) and their derivative (DTG) with respect to temperature corresponding to pyrolytic decomposition of MSWC, at 20ºC min^{-1}

are shown in Figure 2 (for the kinetic parameters calculation four thermograms, at four heating rates 5, 10, 15 and 20ºC min^{-1}, have been carried out. To show the evolution only the last thermogram has been displayed. In this form, the mass loss profile (TGA) and its derivative curve (DTG) obtained by thermogravimetric analysis are shown in Figure 2.

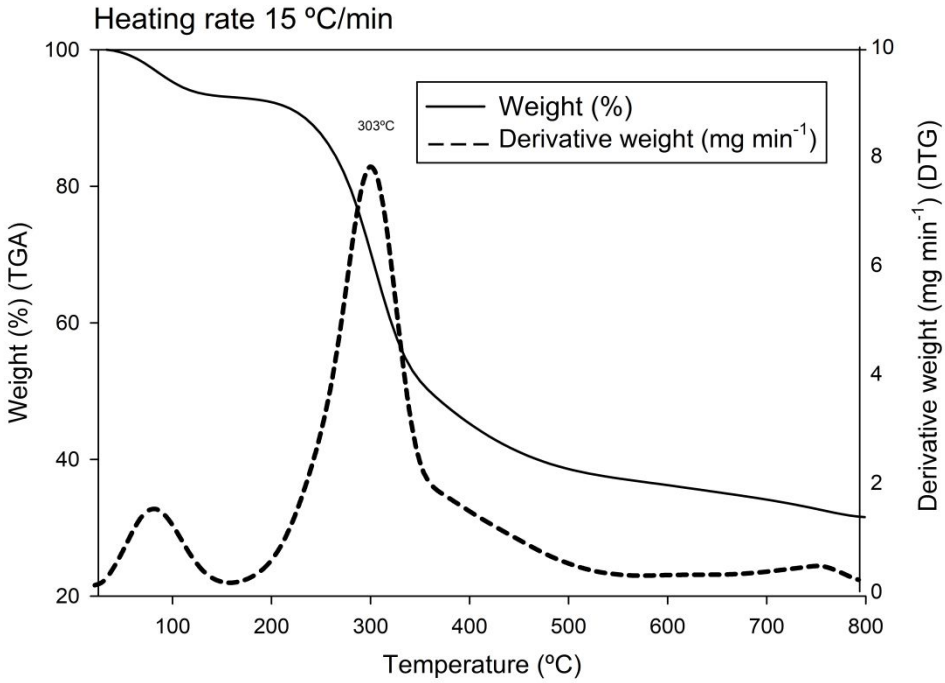

Figure 2. TGA and DTG correspond to MSW Compost pyrolytic degradation at 20ºC min^{-1}.

The figure shows the typical evolution described by different researchers (Dhyani et al., 2018). Similar to what was observed by López-González et al. (2014) in the pyrolysis process of manure compost, a thermochemical behavior similar to that of lignocellulosic biomass can be observed. In this evolution the three main phases in the thermal degradation of compost: phase 1 between 25 and 120 °C; phase II between 200 °C and 400 °C and phase III between 400 °C and 700 °C can be observed. The peak found (DTG) in the first phase (<200ºC) corresponds

to the dehydration process of the compost sample although some authors indicate that decarboxylation may also occur in labile compounds (Pietro and Paola, 2004). The main peak (DTG) in the second phase (200-350 °C) can be identified and a weight loss over 44% at this stage can be calculated. This second peak to the thermal degradation of simple organic matter and semi-volatile compounds such as hemicelluloses, cellulose, degradation of aliphatic structures and microbial cell walls can be associated (Baigorri et al., 2009). The data reported in this study are similar to those presented by Sánchez-Silva et al. (2012) for which a significant weight loss between 210 and 373 °C has been reported. This implies a lower temperature range than that found for the different lignocellulosic biomasses, which are usually between 200 and 450 °C. This fact may be due to the lower lignin content (which is the most thermally stable compound) in compost compared to lignocellulosic biomass. The third phase (350-600 °C, shoulder in the DTG) to the degradation of aromatic structures and organic polymers such as lignin, or synthesized during the compost stabilization process has been associated (Dhyani et al., 2018; Soobhany et al., 2017). Additionally, the peak found at temperatures above 600 °C to the volatilization of the produced biochar and inorganic components (nitrates and carbonates, etc.) has been attributed (Parthasarathy et al., 2021).

The optimum temperature to obtain the maximum yield will vary depending on the feedstock. According to the TGA evolution, with a reactor temperature of 450 °C a degradation of the organic matter in the studied composts without volatilization of the inorganic components can be assured. In this sense, Buah et al. (2007), Agirre et al. (2013), Ansah et al. (2016) experiences of pyrolysis of MSW between 400 and 550 °C have carried out and approximately, between

400-600 °C the optimal temperature range for most lignocellulosic materials has been published (Tagade et al., 2021). Nevertheless, within the optimum range, the operating temperature not only modifies the bio-oil yield but also changes its composition. In this regard, it has been published that under lower temperatures more carbon can be produced while, under temperatures between 500 °C and 550 °C, higher bio-oil yields can be found. Also, at temperatures above 600 °C, the bio-oil yield may decrease and an increase of non-condensable gases may be found (Ansari et al., 2018).

3.2. Compost pyrolysis kinetics

Table 2 shows the results of the application of the FWO method. In this regard, Palma et al. (2020) in a study of the pyrolysis of MSW compost, concluded that adjusting the pyrolysis of MSW compost to first-order kinetics appears to be a suitable approach. A similar trend to that found by other researchers in lignocellulosic biomass (Açıkalın and Gözke, 2021) has been found in the evolution of the Activation Energy of compost. This similar behavior by other authors has been previously described (Fernández-López et al., 2016). Thus, an increase up to values close to 200 kJ mol^{-1} has been found at 20% (α=0.20) conversion.

Conversion (α)	Ea (kJ mol^{-1})	log(A) (log s^{-1})
0.2	211.9	20.6
0.3	191.4	19.7
0.4	222.3	20.0
0.5	301.6	21.1
0.6	150.2	21.5
0.7	85.4	23.3

Table 2. Calculated Activation energy of MSWC under conversion degree (α) by using Flynn-Wall-Ozawa method.

The 20% conversion occurs at 300 °C, at this temperature the degradation of hemicelluloses and cellulose begins. In this respect, Collard and Blin (2014) showed that cellulose pyrolytic degradation occurs mainly between 300 and 400 °C. Also, proteins also decompose at such temperatures (Kebelmann et al., 2013). During this process, Ea remains at similar values up to 50% conversion (α=0.5), which approximately corresponds to 450ºC. At this point, according to Soobhany et al. (2017), with the degradation of aromatic structures, depolymerization of lignin and other organic polymers synthesized during the compost stabilization process (humic and fulvic substances), have been associated and, this fact, can lead to an increase in Ea values to 301.6 kJ mol^{-1}. In this sense, the drop in Ea at the lower values of this parameter for lignin-derived compounds (34.94-122.24 KJ mol^{-1}) (Soh et al., 2019), with respect to those found for cellulosic derivatives (340-360) (Huang et al., 2011), may be due.

The calculated activation energy values are in the range found by other authors (60-600 kJ mol^{-1}) (Fernández-López et al., 2016; Palma et al., 2020). Moreover, Palma et al. (2020) have studied the pyrolysis of MSW compost under two different composting conditions (different aeration and moisture) finding activation energy values in the range of 57.78-581.69 kJ mol^{-1}.

Finally, after the depolymerization processes of the different compounds formed during composting, a drop in Ea has been calculated (to values similar to 150 kJ mol^{-1}) for α>0.6, which can be attributed to the volatilization of residual carbon in

the compost (Dhyani et al., 2018) since the temperatures at which it takes place are higher than 600 °C.

The velocity constant, following the Arrhenius Equation (basis of the Flynn-Wall-Ozawa model) can be expressed as (Eq. 2).

$$k(T) = A \cdot e^{\frac{-Ea}{R \cdot T}}$$ (Eq. 2)

where T is Temperature 450 °C (723 K), R=8.314472 J mol^{-1} K^{-1}. Substituting the maximum values (Table 2) of Ea (301.6 kJ mol^{-1}) and A (21.1 s^{-1}), we can obtain a velocity constant: k=21.1 mol s^{-1}. Therefore, given the high level of degradation that, under the proposed conditions, takes place. At low material addition levels, to the fluidized bed reactor, a complete conversion can be ensured.

3.3. Material Balance

The material was introduced into the pyrolytic reactor at a rate of 1000 g h^{-1}. The operating time was 30 min, thus, 500 g (6% moisture) has been processed.

The biochar yields were 83.55 g (16.71 %) and 40.25 g (8.05%) for cyclones CY1 and CY2, respectively, with moisture contents of 0.83% and 0.18%, respectively. This means almost 25% yield in biochar. In this regard, comparable values for different biomasses by Boateng et al. (2012) (17-28%), Jaroenkhasemmeesuk and Tippayawong (2015) (30%) and Larina and Zaichenko (2018) (35%), under temperatures similar to the studied ones, have been found. Generally, moisture contents lower than 11% in raw materials have little influence on biochar yield (Di Blasi et al., 2000) because a high initial moisture content of the feedstock and a slow heating rate may result in an incomplete devolatilization of the biochar.

In the condensable fraction of pyrolysis (pyrolytic liquids), 162.2 g (32.44%) and 18.35 g (3.67%) yields in condensers CD1 and CD2, respectively, have been found. This means 36.11% yield in condensable fraction. Comparable values

have been found, by Boateng et al. (2012) (10-45%) and Jaroenkhasemmeesuk and Tippayawong (2015) (30%) for different biomasses, although lower than those found by Mohan et al. (2006) (60-75%). According to Ferreira (2000), almost 100% of the intrinsic water in the compost (8%) is responsible for the major part and composition of the liquid found in condensers.

Over 64% increment in water content with respect to the initial water content has been found. This may be due to the reaction that, at the process temperatures, has been taking place between the oxygenated compounds in the compost (being the product of biooxidative reactions) and the hydrogen released during the pyrolytic degradation reactions, resulting in a high water yield.

The measured non-condensable gases was 171.6 g (36.32%) with a moisture content of 0.12%. Thus, a total yield in the balance of 95% was calculated. A wide range 27-73% on bibliography (Boateng et al., 2012) have been found because the condensation time and conditions significantly vary the amount of gas produced. In this regard, a value similar to this study by Jaroenkhasemmeesuk and Tippayawong (2015) (40%) has been found. Although a value higher than that found by Larina and Zaichenko (2018) (15%) and lower than those found by Mohan et al. (2006) (60-75%), has been calculated. The rest at different process points had to be deposited.

3.4. Biochar analysis

The amount of biochar obtained 35.6 ± 3.2 (w.t.) is slightly higher than that found by Ghorbel et al. (2015) who showed a yield of 31% in biochar from farm breeding compost and similar to the yields obtained in biomass pyrolysis (25-40%) at the reaction temperature (Ghodake et al., 2021). The elemental composition of the resulting biochar in Table 3 is shown. Moreover, the ash content of the resulting

biochars increased significantly with respect to the feedstock ash due to the loss of organic matter which, during the pyrolysis process, passes into the gas phase. Similarly, the carbon content in the biochar increased by 8.6% with respect to the original compost. The progressive concentration of carbon and minerals during volatilization produced by increasing temperatures can cause this process.

	C (%)	H (%)	O (%)	S (%)
Cyclon 1 (CY1)	46.6 ± 2.7	1.62 ± 0.3	51.2 ± 2.3	0.54 ± 0.1
Cyclon 2 (CY2)	48.7 ± 1.9	1.84 ± 0.5	48.9 ± 2.0	0.51 ± 0.1

[a] Mean values and standard deviations were calculated from the triplicates

Table 3. Chemical characteristics of obtained biochar[a].

The H/C and O/C ratios to estimate the stability of biochar in soil are commonly used. O/C ratio may be a suitable indicator of biochar stability and may inform about the general polarity of the material (Shakya and Agarwal, 2017). The O/C ratio the abundance of polar oxygen-containing surface functional groups in biochar can indicate (Rangabhashiyam and Balasubramanian, 2019). Therefore, high values indicate a higher polarity of functional groups. Alternatively, low O/C ratios, because the adsorption mechanism shifts from being mainly based on ion exchange to physisorption (Ahmad et al., 2012), low adsorption capacity may indicate due to the weaker nature of physisorption. In this study, high O/C ratios >0.6 (0.9-1.0) have been found and these data may be indicative of a product that is not very stable in soil and therefore, low stability of the biochar produced can be assumed.

On the other hand, H/C ratio the aromaticity and stability of the biochar (Wei et al., 2020; Xiao et al., 2016) may indicate. Low values for this parameter have been found, therefore a low aromaticity can be shown.

These data, with respect to different biomasses, are shown in Figure 3. Differences, mainly in the H/C ratio, with respect to other biochar have been found. This may be due to the loss of aromatic structures that during composting (Joyce et al., 1998), due to the previous microbological action, has taken place and that may have caused the differences with respect to other biochar from original biomass.

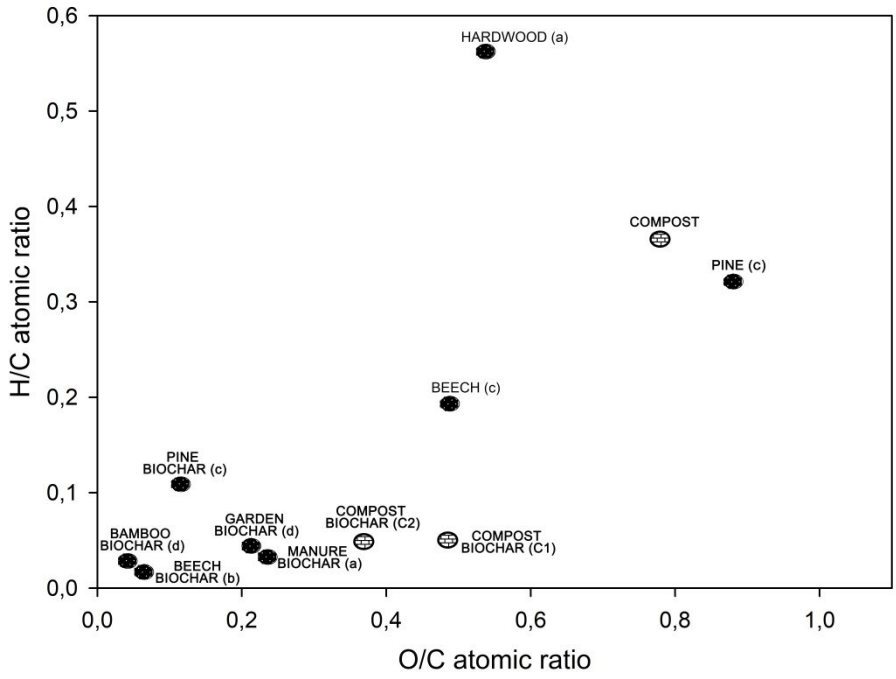

Figure 3. Van Kreveren graph (H/C vs O/C atomic ratio) for the obtained compost biochar with respect to other raw materials ([a]Fabbri et al. (2012); [b]Morin et al. (2016); [c]Guizani et al. (2017); [d]Dang et al. (2021).

Low values of gross heating, 14.18 and 18.56 MJ kg^{-1} for C1 and C2 samples, respectively, have been found. Values similar to 25-30 MJ kg^{-1} in biochars from

different feedstocks have been found (Jiang et al., 2018; Tsai et al., 2018), but higher than those found by Mierzwa-Hersztek et al. (2019), in the range of 11-12 MJ kg^{-1} for sawdust, wheat straw, and miscanthus straw. In this regard, Tripathi et al. (2016) showed that the calorific value of biochar is directly proportional to the process temperature and inversely proportional to the H/C and O/C molar ratios. The obtained data supports the conclusions drawn by these authors.

Alkalinity is one of the most influential properties of biochar, because changes in pH have large impact on many soil processes (Fidel et al., 2017). In this study, values of 12.04 and 12.37 have been found for C1 and C2, respectively. In this regard, Li et al. (2013) and Fidel et al. (2017) showed values between 5.5-10.3 depending on the biochar feedstock and pyrolysis conditions. The values found in biochar from MSW compost, are higher than those found by the previous authors. This fact may be due to the high amount of basic salts usually found in MSW compost (Xie et al., 2020) that give rise to a basic pH already in the original compost and that are concentrated by the pyrolysis process in the biochar obtained since the process conditions (450ºC) do not cause the volatilization of these salts.

3.5. Bio-oil GC/MS analysis

The bio-oil obtained from the pyrolysis of compost at 450 °C for 30 min in a fluidized bed reactor was analyzed by GC-MS and are shown in Table 4. Since the compost is formed mainly by lignocellulosic material composed of cellulose, hemicellulose and lignin, the pyrolysis products are derived from these components in different proportions. Numerous chemical compounds have been obtained in bio-oils but the complete identification is complex, with 24 of the most important compounds identified and studied in depth.

The main cellulose decomposition compound in compost pyrolysis as furan-2-ylmethanol (3.3%) and as nitrogenous product is found 5-(hydroxymethyl)-1-methylpyrrolidin-2-one (2.4%) have been found. As shown in Table 4, the phenolic compounds typical in lignin disintegration, such as methylphenols (12.7%), 2-methoxyphenol, better known as guaiacol (6.9%), 4-methylbenzene-1,2-diol (5.7%) or 3-(2-hydroxyethyl)phenol (6.4%) have been found among many others, assuming more than 80% of the total of degraded products.

The low concentration of short-chain compounds common of the fragmentation of cellulose and hemicellulose such as carbohydrates highlighting the levoglucosan in the pyrolytic liquids (Kim et al., 2013) compared to untreated lignocellulosic biomass reveals the decomposition of these components in the composting process, making more complex lignin compounds attract attention to a greater extent.

Compounds	Formula	MS	RT (min)	Area (%)
Ethane-1,2-diol	$C_2H_6O_2$	62.07	12.591	2.45
Furan-2-ylmethanol	$C_5H_6O_2$	98.10	12.904	3.29
Phenol	C_6H_6O	94.11	14.288	6.32
5-(hydroxymethyl)-1-methylpyrrolidin-2-one	$C_6H_{11}NO_2$	129.16	15.653	2.44
2-methylphenol	C_7H_8O	108.14	16.050	3.30
3-methylphenol	C_7H_8O	108.14	16.220	4.58
4-methylphenol	C_7H_8O	108.14	16.444	4.82
3-methylcyclohex-1-en-1-ol	$C_7H_{12}O$	112.17	17.558	6.19
2-methoxyphenol	$C_7H_8O_2$	124.14	18.088	6.29
3-ethylphenol	$C_8H_{10}O$	122.16	18.272	2.11
benzene-1,3,5-triol	$C_6H_6O_3$	126.11	19.040	3.08
2-methoxy-5-methylphenol	$C_8H_{10}O_2$	138.16	19.862	3.34
benzene-1,4-diol	$C_6H_6O_2$	110.11	19.938	3.73
3-methylbenzene-1,2-diol	$C_7H_8O_2$	124.12	21.265	2.68
methyl 3-hydroxybenzoate	$C_8H_8O_3$	152.15	21.321	5.36
2,6-dimethoxyphenol	$C_8H_{10}O_3$	154.16	21.450	3.26

4-methylbenzene-1,2-diol	$C_7H_8O_2$	124.14	21.528	5.69
1-(2-hydroxyphenyl)propan-1-one	$C_9H_{10}O_2$	150.17	22.122	5.06
3-(2-hydroxyethyl)phenol	$C_8H_{10}O_2$	138.16	22.528	6.39
2-methoxy-4-propylphenol	$C_{10}H_{14}O_2$	166.22	22.685	4.62
1-(2-hydroxy-6-methoxyphenyl)ethanone	$C_9H_{10}O_3$	166.17	23.553	4.67
2-methoxy-4-prop-2-enylphenol	$C_{10}H_{12}O_2$	164.20	23.861	2.15
1-(4-hydroxy-3-methoxyphenyl)ethanone	$C_9H_{10}O_3$	166.17	24.359	6.01
4-(3-hydroxypropyl)-2-methoxyphenol	$C_{10}H_{14}O_3$	182.22	28.106	2.15

Table 4. Main compounds found by GC/MS in bio-oil of MSW compost pyrolysis at 450ºC.

3.6. Non-condensable gases GC/MS analysis

The volatile organic pyrolysis products that are found in a small proportion mixed with mainly nitrogen and other light gases detected by GC/MS are shown in Table 5. In this case, the non-condensable gases contain compounds derived from hemicellulose and cellulose, among other compounds of composted urban waste that barely appeared in pyrolytic liquids.

Compounds	Formula	MS	RT (min)	Area (%)
2-methylpropan-1-ol	$C_4H_{10}O$	74.12	4.140	5.27
1-pentanol	$C_5H_{12}O$	88.15	4.255	4.69
pent-1-en-3-yne	C_5H_6	66.10	4.320	2.93
2-methylpropanal	C_4H_8O	72.11	4.425	3.40
hexanal	$C_6H_{11}O$	100.16	4.660	5.04
2,2-dimethylpropanenitrile	C_5H_9N	83.13	4.965	3.37
(3E)-hexa-1,3,5-triene	C_6H_8	80.13	5.195	5.25
4-methylpenta-1,3-diene	C_6H_{10}	82.14	5.315	3.60
hexa-1,5-diyne	C_6H_6	78.11	5.470	3.82
(3E)-hexa-3,5-dien-2-ol	$C_6H_{10}O$	98.14	5.565	4.04
2,2-dimethylpropanal	$C_5H_{10}O$	86.13	5.935	5.48
2-methylpent-4-en-1-ol	$C_6H_{12}O$	100.16	5.990	2.60
2,5-dimethylfuran	C_6H_8O	96.13	6.130	4.45

(5E)-hepta-1,5-diene	C_7H_{12}	96.17	6.510	3.75
ethenyl acetate	$C_4H_6O_2$	86.09	6.665	4.80
5-methylhexa-1,4-diene	C_7H_{12}	96,17	6.985	5.18
(3E)-2-methylhexa-1,3,5-triene	C_7H_{10}	94.15	7.115	4.64
3-prop-2-enylcyclopentene	C_8H_{12}	108.18	7.270	5.25
(5E)-hepta-1,5-dien-3-yne	C_7H_8	92.14	7.755	4.98
cyclopentanone	C_5H_8O	84.12	8.340	4.35
octane	C_8H_{18}	114.23	8.595	3.59
methyl 2-methylpropyl carbonate	$C_6H_{12}O_3$	132.16	10.545	2.75
1,3-xylene	C_8H_{10}	106.16	10.715	3.29
1,2-xylene	C_8H_{10}	106.16	10.965	3.47

Table 5. Main compounds found by GC/MS in non-condensable gases of MSW compost pyrolysis at 450ºC.

A significant amount of alcohols (16.6%) is found in organic gases, such as 2-methylpropan-1-ol (5.3%), 1-pentanol (4.7%), (3E)-hexa-3,5-dien-2-ol (4.0%) or 2-methylpentent-4-en-1-ol (2.6%). There is also a wide variety of aldehydes (13.9%) such as 2-methylpropanal (3.4%), hexanal (5.0%) or 2,2-dimethylpropanal (5.5%). Some compounds derived from hemicellulose and cellulose are also observed, mainly 2,5-dimethylfuran (4.5%). The same compound was also found by Hubble and Goldfarb (2021) in hemicelluloses pyrolytic degradation. A group of compounds derived from plastics and other compounds of more specific urban solid waste can be distinguished, as in the case of 1,3-xylene and 1,2-xylene (3.3% and 3.5%, respectively).

It should be noted that numerous organic compounds with double and triple bonds (36.6%) are obtained from the degradation of carbohydrates, proteins and other typical components of organic matter of animal or human origin (Somorin et al., 2020). The compost has been produced from solid urban waste from

coastal area and is made up of various remains of seashells and bones, so these chemical compounds from its decomposition are common.

4. Conclusions

The behaviour of MSW compost and products formed in fluidized bed pilot plant is similar to that established on lignocellulosics raw material. Four characteristic zones (humidity evolution, hemicellulose decomposition, lignin and cellulose degradation and lignin disintegration) have been found.

The TGA evolution and its kinetic constants similar to those found for lignocellulosic materials have been measured. However, the produced biochar has low stability and aromaticity due to its high and low O/C and H/C ratios, respectively. Additionally, the compounds found in the bio-oil as highly phenolics can be described, it could be due to its humic and fulvic compounds (heavy compounds) in the original material (compost) as well as lignin not degraded during the composting process. Moreover, the compounds in non-condensable gases to thermal degradation of shorter structures such as hemicellulose, proteins and cellulose may be due.

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Pyrolysis of Municipal Solid Waste compost: pilot plant evaluation as a sustainable practise of waste management

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Abstract

To evaluate the potential of compost based on Municipal Solid Waste (MSW) and 20% legume pruning under a pyrolysis process, generated products, including solids (biochar), liquids (bio-oil) and gases (non-condensable gases), through experimentation in a pilot plant with a fluidised bed reactor at 450 °C and gas chromatography/mass spectrometry (GC/MS) have been analysed. Also, the compost kinetic behaviour by thermogravimetric analysis (TGA), using Flynn-Wall-Ozawa method, has been investigated. Four different reaction zones, associated with lignocellulosic materials (hemicellulose, cellulose and lignin) with a first step for water evaporation, in TGA curve have been observed. A biochar with low stability and aromaticity, considering high and low O/C and H/C ratios, respectively, has been obtained. The obtained pyrolytic liquids contain a high concentration of phenolic compounds because of a significant presence of lignins and other high molecular weight compounds in the original material. Moreover, the generated non-condensable gases consist mainly of short-chain compounds such as alcohols, aldehydes and alkenes produced from hemicellulose, cellulose and proteins.

Keywords: pyrolysis; MSW compost; kinetic; GC/MS; biochar.

1. Introduction

It has been widely recognised that inadequate treatment of organic waste can lead to significant environmental and health problems. In this respect, the beneficial properties of compost both as a suitable solution for the treatment and sanitation of organic waste and its subsequent use in agriculture (both technically and economically) have been extensively demonstrated (Rashid and Shahzad, 2021). Despite the problems that inadequate management, mainly due to the odours emitted (Delgado-Rodríguez et al., 2011) can cause.

The quality of the final compost will depend significantly on the nature and quality of the waste to be composted. However, the process parameters are also involved in the degradation to which the organic compounds are subjected during composting. Therefore, a high variability of quality in the produced compost can be ascertained, and quality standards for its use in agriculture must be applied (Hameed et al., 2021). However, in addition to the traditional uses of compost, new uses and organo-mineral formulations (Fachini et al., 2021) are being developed.

In the EU-28 (28 EU Member States) approximately 88 million tonnes/year of food are wasted. About 20% of the food produced represents this value. Because of various problems, including lack of segregated sorting and impurities, only 17% of this municipal waste can be properly composted and/or digested (EEA, 2020). Therefore, a high proportion of composted Municipal Solid Waste (MSW) is not of a quality suitable for direct use in agriculture.

Consequently, various ways of valorization of this compost of low agronomic quality, apart from the alternative uses that are already being used, such as the recovery of degraded areas (mines, quarries, landfills), forestry crops, etc.,

should be explored. Therefore, enhancing the valorisation pathways of these materials to improve the management of these wastes should be developed.

Thermochemical processes, due to the wide range of products (solid, liquid and gaseous) and/or energy generated, are an alternative to be considered for the valorisation of organic materials. Among these, combustion (with an excess of oxygen over that required according to stoichiometry), gasification (with a deficit of oxygen over that required according to stoichiometry) and pyrolysis (without oxygen) can be noted (Beis et al., 2002).

In this sense, pyrolytic processes as a source of new high value-added products from compost can be highlighted. During composting, organic compounds are generally degraded or directly mineralized, although a portion of the high molecular weight compounds present in the original material increase the degree of aromaticity in the resulting composted compounds. Also, an increase in the mass degradation above 600 °C as the composting time increases (Díaz et al., 2021) is produced. Thus, the composting process significantly alters the distribution of chemical compounds and may result in products that may not be produced during pyrolysis of other sources of organic compounds.

Among these innovative materials from compost by pyrolysis, Qian et al. (2007) and Finney et al. (2009) used compost, from livestock manure and mushroom industry residues, respectively, as raw material for the production of biochar. Also, the use of composts, in the pyrolysis process, as a potential feedstocks for bio-oil production has been studied by Garrido et al. (2012) and Giwa et al. (2018).

The general objective of this work is to study the products generated (biochar, pyrolytic liquids and volatile organic compounds) during the pyrolysis of MSW

compost with 20% pruning residues. Also, the kinetics of the reactions produced during the pyrolysis of these composts has been studied.

2. Materials and Methods

2.1. MSW composition

The different components of MSW can be classified into three main groups: fermentable (food waste), combustible (paper, cardboard, plastics, rubber, textiles, wood, etc.), and inert (metals, glass, etc.). The composition of MSW is highly variable and depends on factors such as the standard of living, lifestyle of the population, and the time of year. The composition of the MSW composted in this study is shown in Figure 1.

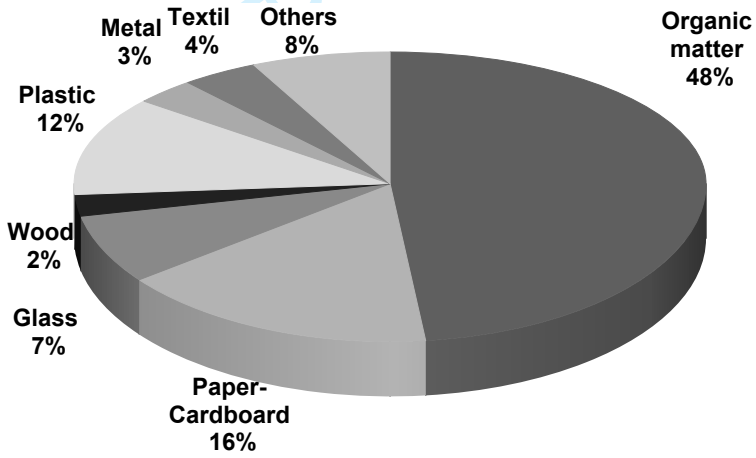

Figure 1. MSW composition.

2.2. Compost characteristics

Non-selective Municipal Solid Waste Compost (MSWC) from Villarrasa (Huelva - Spain) urban waste treatment plant is used in this study. Prior to composting the main treatment involves trammel-screening (8 cm), metal electromagnetic separation and manual separation of plastics. To improve internal aeration in composting piles, 20% of bulking material (legume pruning of *Leucaena*

leucocephala), before the composting process, have been added. The non-degraded fraction of this material was separated by screening at the end of the composting process. The most relevant chemical characteristics of the final compost are reported in Table 1.

Property	Units	Compost (after 40 days)
pH (1:5 extract)		7.8 ± 1.2
EC (1:5 extract)	dS m^{-1}	8.5 ± 1.1
Organic Matter	g kg^{-1}	593 ± 32
Kjeldahl-N	g kg^{-1}	12.3 ± 3.5
Ash	g kg^{-1}	35.4 ± 4.7
C/N		26.6
Moisture	%	0.6

[a] Determined in MSW <5 mm and free of impurities
[b] Mean values and standard deviations were calculated from the triplicates

Table 1. Relevant characteristics of used MSWC[a] (average ± standard deviation)[b]

2.3. Processing of the samples by pyrolysis with TGA

The dried compost samples, with an initial average diameter of 50 mm, were milled into particles of smaller size (1-2 mm). The final particles were stored without contact with air moisture. Thermochemical decomposition behavior was evaluated using a thermo-gravimetric analyzer (TGA) (Mettler Toledo TGA/DSC1 STARe System). TGA experiments heating 10-25 mg samples from 25 °C to 850 °C, at four heating rates (5, 10, 15 and 20 °C min^{-1}) under nitrogen flow rate of 20 cm^3 min^{-1} have been performed. The obtained thermo-gravimetric analysis data

for any changes in the thermo-chemical decomposition behavior have been studied.

2.4. Pilot plant pyrolysis

A laboratory-scale fluidized bed reactor (PID Eng&Tech Micromeritics) has been employed. An operating temperature of 450 °C has been used. 30 L min^{-1} of nitrogen (twice the minimum fluidization rate) has been used, with a constant pressure difference of 33 mbar.

A gas cleaning system at the reactor outlet has been installed. This system consists of two cyclones (CY1 for particles >20μm and CY2 for particles >5μm) that have been connected in series. Downstream, a heat exchanger (400ºC to 90ºC), controlled by a single valve, is used to regulate the inflow of the coolant fluid (water 20ºC) into the heat exchanger. Pyrolytic liquids in a cooling vessel (first condenser (CD1) at 63 °C), located at the bottom of the heat exchanger have been collected. Water and other condensed liquids are retained in a second condenser (CD2) (30ºC). Finally, the product gases pass through coalescing filters before sampling and finally into a scrubber (23ºC).

2.5. Pyrolytic liquid analysis

An aliquot to pyrolytic liquid has been extracted with water (1:10 ratio), vortexed 30 s and centrifugation for 20 min at 5000 rpm. Then, 1 mL the water-insoluble fraction was extracted with diethyl ether (DEE) (3 x 1 mL). After extraction, an aliquot DEE extract (500 μL) has been dried under nitrogen and 50 μL of both pyridine and BSTFA/TMCS (90:10) were added following incubated for 30 min at 60ºC. Then, TMS derivative extracts were diluted (1:10) with $CHCl_3$ and 1 μL was injected into GC-MS/MS (GCMSQP8030 Ultra System, Shimadzu, Japan). TMS derivative compounds were separated by a HP-5 MS column (60 m, 0.25 mm I.D.

0.25 µm film thickness, J&W Scientific, Agilent Technologies, USA). The GC oven was programmed: 50 °C for 2 min, ramped at 8 °C min^{-1} to 280 °C, held for 2 min. A second ramp rate was performed of 50 °C min^{-1} until a final temperature of 300 °C was reached and held for 2 min. Helium at constant flow rate of 1.20 mL min^{-1} was used as the carrier gas. The temperatures of the injection port (split mode 10:1), transfer line and ion source were maintained at 250, 280 and 230 °C, respectively. The mass spectrometer was operated in scan mode (50-800 m z^{-1}). TMS derivative compounds were identified by comparison of the mass spectra with those of the database of NIST11 library. For control and data analysis, GCMS Postrun Analysis Shimadzu was used. The MS was turned with perfluorotributylamine (PFTBA).

2.6. Biochar analysis

Gross Calorific Value (constant volume) following the standards "CEN/TS 14918:2005 (E) Solid Biofuels - Method for the determination of the calorific value" and UNE 164001 EX have been determined. Automatic Isoperibol Calorimeter Parr 6300 has been used. Total carbon, hydrogen and sulphur simultaneously in a ELTRA Carbon/Hydrogen/Sulfur Analyzer CHS-580A (ELTRA GmbH, Germany) have been determined. The standard guidelines for the determination of carbon, hydrogen (EN 15104:2011) and sulfur (EN 15289:2011) have been followed. Moreover, oxygen content by difference (CEN/TS 14961, 2005) has been also calculated. According to ISO 10390:2005, biochar was air-dried and crushed into fine particles (<2 mm). Then, the sample was soaked with 0.01 M $CaCl_2$ at a 1:5 solid/water ratio for 1 h with agitation.

After still standing for 1 h, the slurry was then measured for pH using a pH-meter GLP 21 (Crison Instruments, S.A.).

2.7. Volatile compounds gas samples analysis by pyrolysis TD/GC-MS

Volatile compounds gas samples from the pilot plant pyrolysis process at 350 and 550ºC (corresponding to higher temperatures than the degradation maxima found in the TGA curves) were collected in fritted glass TD tubes (Supelco, Bellefonte, PA; O.D.: 6.35 mm; length: 88.9 mm) for 1.5 min. Tubes containing 100 mg of Tenax® TA (80-100 mesh purchased from Supelco, Bellefonte, PA) packed in layers of silanized glass wool. TD tubes after sampling have been analyzed using TD/GC-MS. TD was used to release the captured volatile compounds from the tube sorbent material onto the GC/MS for identification and quantification. TD was carried out by use of thermal desorption system unit (TD-20, Shimadzu, Japan) fitted with a HP-5 MS column (60 m, 0.25 mm I.D. 0.25 µm film thickness, J&W Scientific, Agilent Technologies, USA) and involved 2 steps: tube desorption and trap desorption. The mass spectrometer was operated in scan mode (41-450 m z^{-1}). Volatile organic compounds were identified by comparison of the mass spectra with those of in the database of NIST11 library using as internal standard 1-bromo-3-chlorobenzene (BCB). For control and data analysis, the GCMS Postrun Analysis Shimadzu was used. The MS was turned with perfluorotributylamine (PFTBA).

2.8. Kinetic analysis by Flynn-Wall-Ozawa method

The activation energy of pyrolysis reactions in lignocellulosic materials has been studied by several different mathematical methods. In this regard, the use of isoconversional methods for the determination of pyrolysis kinetics has been successfully documented (Açıkalın and Gözke, 2021). Moreover, according to the

results obtained by Fernández-López et al. (2016) and Palma et al. (2020), this model has been satisfactorily tested in different composts. Moreover, Gunasee et al. (2016) have demonstrated that this TGA-based experimental methodology could be suitable for revealing synergistic reactions during co-pyrolysis of different MSW.

For a given reaction, the activation energy should be a constant value throughout the weight loss region, so changes in these values imply degradation of other compounds. In the present study the activation energy values for the degradation process using the Flynn-Wall-Ozawa (FWO) isoconversional method (Flynn and Wall, 1966; Ozawa, 1965) defined by Eq. 1 have been determined. This method for determination of the Ea values without any knowledge of its mechanisms (El-Sayed and Mostafa, 2015) can be used.

$$ln\,(\beta) = ln(\frac{A\,Ea}{R\,g(\alpha)}) - 2.315 - 0.4567\,\frac{Ea}{R\,T} \quad \text{(Eq. 1)}$$

where β is the heating rate, A is the pre-exponential factor, g(α) is a function of the conversion, E_a is the activation energy and R is the gas constant.

Therefore, for different heating rates (β) and a given degree of conversion (α), a linear relationship is observed by plotting of natural logarithm of heating rates (ln β), versus (1/T) obtained from thermal curves recorded at different heating rates will be a straight line whose slope (–0.4567 (E_a/RT)) will calculate the activation energy.

3. Result and Discussion

3.1. Compost TGA analysis

Thermograms of compost (TGA) and their derivative (DTG) with respect to temperature corresponding to pyrolytic decomposition of MSWC, at 20ºC min^{-1}

are shown in Figure 2 (for the kinetic parameters calculation four thermograms, at four heating rates 5, 10, 15 and 20ºC min^{-1}, have been carried out. To show the evolution only the last thermogram has been displayed. In this form, the mass loss profile (TGA) and its derivative curve (DTG) obtained by thermogravimetric analysis are shown in Figure 2.

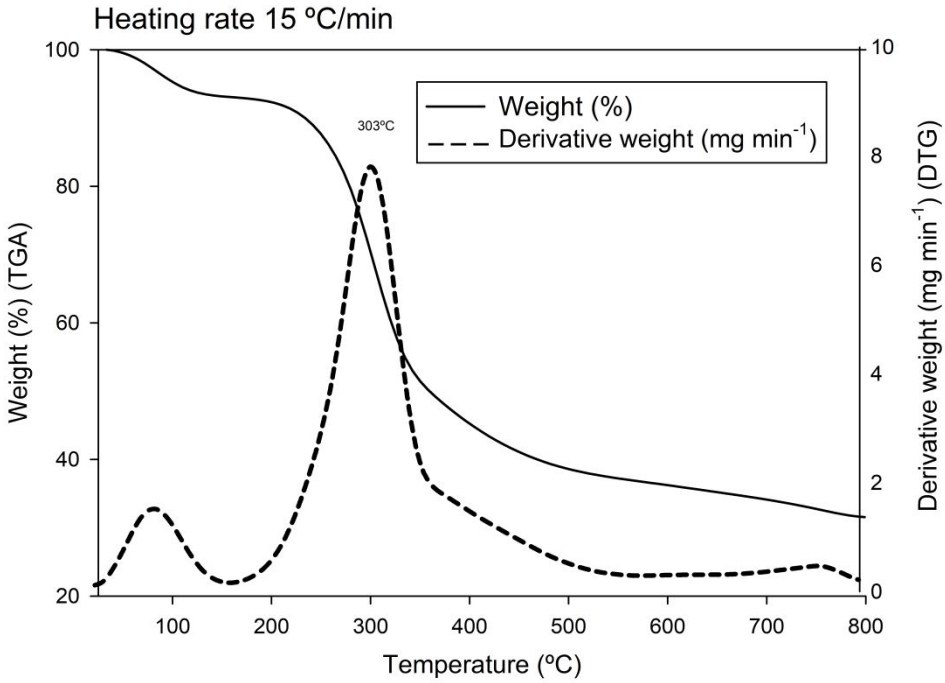

Figure 2. TGA and DTG correspond to MSW Compost pyrolytic degradation at 20ºC min^{-1}.

The figure shows the typical evolution described by different researchers (Dhyani et al., 2018). Similar to what was observed by López-González et al. (2014) in the pyrolysis process of manure compost, a thermochemical behavior similar to that of lignocellulosic biomass can be observed. In this evolution the three main phases in the thermal degradation of compost: phase 1 between 25 and 120 °C; phase II between 200 °C and 400 °C and phase III between 400 °C and 700 °C can be observed. The peak found (DTG) in the first phase (<200ºC) corresponds

to the dehydration process of the compost sample although some authors indicate that decarboxylation may also occur in labile compounds (Pietro and Paola, 2004). The main peak (DTG) in the second phase (200-350 °C) can be identified and a weight loss over 44% at this stage can be calculated. This second peak to the thermal degradation of simple organic matter and semi-volatile compounds such as hemicelluloses, cellulose, degradation of aliphatic structures and microbial cell walls can be associated (Baigorri et al., 2009). The data reported in this study are similar to those presented by Sánchez-Silva et al. (2012) for which a significant weight loss between 210 and 373 °C has been reported. This implies a lower temperature range than that found for the different lignocellulosic biomasses, which are usually between 200 and 450 °C. This fact may be due to the lower lignin content (which is the most thermally stable compound) in compost compared to lignocellulosic biomass. The third phase (350-600 °C, shoulder in the DTG) to the degradation of aromatic structures and organic polymers such as lignin, or synthesized during the compost stabilization process has been associated (Dhyani et al., 2018; Soobhany et al., 2017). Additionally, the peak found at temperatures above 600 °C to the volatilization of the produced biochar and inorganic components (nitrates and carbonates, etc.) has been attributed (Parthasarathy et al., 2021).

The optimum temperature to obtain the maximum yield will vary depending on the feedstock. According to the TGA evolution, with a reactor temperature of 450 °C a degradation of the organic matter in the studied composts without volatilization of the inorganic components can be assured. In this sense, Buah et al. (2007), Agirre et al. (2013), Ansah et al. (2016) experiences of pyrolysis of MSW between 400 and 550 °C have carried out and approximately, between

400-600 °C the optimal temperature range for most lignocellulosic materials has been published (Tagade et al., 2021). Nevertheless, within the optimum range, the operating temperature not only modifies the bio-oil yield but also changes its composition. In this regard, it has been published that under lower temperatures more carbon can be produced while, under temperatures between 500 °C and 550 °C, higher bio-oil yields can be found. Also, at temperatures above 600 °C, the bio-oil yield may decrease and an increase of non-condensable gases may be found (Ansari et al., 2018).

3.2. Compost pyrolysis kinetics

Table 2 shows the results of the application of the FWO method. In this regard, Palma et al. (2020) in a study of the pyrolysis of MSW compost, concluded that adjusting the pyrolysis of MSW compost to first-order kinetics appears to be a suitable approach. A similar trend to that found by other researchers in lignocellulosic biomass (Açıkalın and Gözke, 2021) has been found in the evolution of the Activation Energy of compost. This similar behavior by other authors has been previously described (Fernández-López et al., 2016). Thus, an increase up to values close to 200 kJ mol^{-1} has been found at 20% (α=0.20) conversion.

Conversion (α)	Ea (kJ mol^{-1})	log(A) (log s^{-1})
0.2	211.9	20.6
0.3	191.4	19.7
0.4	222.3	20.0
0.5	301.6	21.1
0.6	150.2	21.5
0.7	85.4	23.3

Table 2. Calculated Activation energy of MSWC under conversion degree (α) by using Flynn-Wall-Ozawa method.

The 20% conversion occurs at 300 °C, at this temperature the degradation of hemicelluloses and cellulose begins. In this respect, Collard and Blin (2014) showed that cellulose pyrolytic degradation occurs mainly between 300 and 400 °C. Also, proteins also decompose at such temperatures (Kebelmann et al., 2013). During this process, Ea remains at similar values up to 50% conversion (α=0.5), which approximately corresponds to 450ºC. At this point, according to Soobhany et al. (2017), with the degradation of aromatic structures, depolymerization of lignin and other organic polymers synthesized during the compost stabilization process (humic and fulvic substances), have been associated and, this fact, can lead to an increase in Ea values to 301.6 kJ mol^{-1}. In this sense, the drop in Ea at the lower values of this parameter for lignin-derived compounds (34.94-122.24 KJ mol^{-1}) (Soh et al., 2019), with respect to those found for cellulosic derivatives (340-360) (Huang et al., 2011), may be due.

The calculated activation energy values are in the range found by other authors (60-600 kJ mol^{-1}) (Fernández-López et al., 2016; Palma et al., 2020). Moreover, Palma et al. (2020) have studied the pyrolysis of MSW compost under two different composting conditions (different aeration and moisture) finding activation energy values in the range of 57.78-581.69 kJ mol^{-1}.

Finally, after the depolymerization processes of the different compounds formed during composting, a drop in Ea has been calculated (to values similar to 150 kJ mol^{-1}) for α>0.6, which can be attributed to the volatilization of residual carbon in

the compost (Dhyani et al., 2018) since the temperatures at which it takes place are higher than 600 °C.

The velocity constant, following the Arrhenius Equation (basis of the Flynn-Wall-Ozawa model) can be expressed as (Eq. 2).

$$k(T) = A \cdot e^{\frac{-Ea}{R \cdot T}}$$ (Eq. 2)

where T is Temperature 450 °C (723 K), R=8.314472 J mol^{-1} K^{-1}. Substituting the maximum values (Table 2) of Ea (301.6 kJ mol^{-1}) and A (21.1 s^{-1}), we can obtain a velocity constant: k=21.1 mol s^{-1}. Therefore, given the high level of degradation that, under the proposed conditions, takes place. At low material addition levels, to the fluidized bed reactor, a complete conversion can be ensured.

3.3. Material Balance

The material was introduced into the pyrolytic reactor at a rate of 1000 g h^{-1}. The operating time was 30 min, thus, 500 g (6% moisture) has been processed.

The biochar yields were 83.55 g (16.71 %) and 40.25 g (8.05%) for cyclones CY1 and CY2, respectively, with moisture contents of 0.83% and 0.18%, respectively. This means almost 25% yield in biochar. In this regard, comparable values for different biomasses by Boateng et al. (2012) (17-28%), Jaroenkhasemmeesuk and Tippayawong (2015) (30%) and Larina and Zaichenko (2018) (35%), under temperatures similar to the studied ones, have been found. Generally, moisture contents lower than 11% in raw materials have little influence on biochar yield (Di Blasi et al., 2000) because a high initial moisture content of the feedstock and a slow heating rate may result in an incomplete devolatilization of the biochar.

In the condensable fraction of pyrolysis (pyrolytic liquids), 162.2 g (32.44%) and 18.35 g (3.67%) yields in condensers CD1 and CD2, respectively, have been found. This means 36.11% yield in condensable fraction. Comparable values

have been found, by Boateng et al. (2012) (10-45%) and Jaroenkhasemmeesuk and Tippayawong (2015) (30%) for different biomasses, although lower than those found by Mohan et al. (2006) (60-75%). According to Ferreira (2000), almost 100% of the intrinsic water in the compost (8%) is responsible for the major part and composition of the liquid found in condensers.

Over 64% increment in water content with respect to the initial water content has been found. This may be due to the reaction that, at the process temperatures, has been taking place between the oxygenated compounds in the compost (being the product of biooxidative reactions) and the hydrogen released during the pyrolytic degradation reactions, resulting in a high water yield.

The measured non-condensable gases was 171.6 g (36.32%) with a moisture content of 0.12%. Thus, a total yield in the balance of 95% was calculated. A wide range 27-73% on bibliography (Boateng et al., 2012) have been found because the condensation time and conditions significantly vary the amount of gas produced. In this regard, a value similar to this study by Jaroenkhasemmeesuk and Tippayawong (2015) (40%) has been found. Although a value higher than that found by Larina and Zaichenko (2018) (15%) and lower than those found by Mohan et al. (2006) (60-75%), has been calculated. The rest at different process points had to be deposited.

3.4. Biochar analysis

The amount of biochar obtained 35.6 ± 3.2 (w.t.) is slightly higher than that found by Ghorbel et al. (2015) who showed a yield of 31% in biochar from farm breeding compost and similar to the yields obtained in biomass pyrolysis (25-40%) at the reaction temperature (Ghodake et al., 2021). The elemental composition of the resulting biochar in Table 3 is shown. Moreover, the ash content of the resulting

biochars increased significantly with respect to the feedstock ash due to the loss of organic matter which, during the pyrolysis process, passes into the gas phase. Similarly, the carbon content in the biochar increased by 8.6% with respect to the original compost. The progressive concentration of carbon and minerals during volatilization produced by increasing temperatures can cause this process.

	C (%)	H (%)	O (%)	S (%)
Cyclon 1 (CY1)	46.6 ± 2.7	1.62 ± 0.3	51.2 ± 2.3	0.54 ± 0.1
Cyclon 2 (CY2)	48.7 ± 1.9	1.84 ± 0.5	48.9 ± 2.0	0.51 ± 0.1

[a] Mean values and standard deviations were calculated from the triplicates

Table 3. Chemical characteristics of obtained biochar[a].

The H/C and O/C ratios to estimate the stability of biochar in soil are commonly used. O/C ratio may be a suitable indicator of biochar stability and may inform about the general polarity of the material (Shakya and Agarwal, 2017). The O/C ratio the abundance of polar oxygen-containing surface functional groups in biochar can indicate (Rangabhashiyam and Balasubramanian, 2019). Therefore, high values indicate a higher polarity of functional groups. Alternatively, low O/C ratios, because the adsorption mechanism shifts from being mainly based on ion exchange to physisorption (Ahmad et al., 2012), low adsorption capacity may indicate due to the weaker nature of physisorption. In this study, high O/C ratios >0.6 (0.9-1.0) have been found and these data may be indicative of a product that is not very stable in soil and therefore, low stability of the biochar produced can be assumed.

On the other hand, H/C ratio the aromaticity and stability of the biochar (Wei et al., 2020; Xiao et al., 2016) may indicate. Low values for this parameter have been found, therefore a low aromaticity can be shown.

These data, with respect to different biomasses, are shown in Figure 3. Differences, mainly in the H/C ratio, with respect to other biochar have been found. This may be due to the loss of aromatic structures that during composting (Joyce et al., 1998), due to the previous microbological action, has taken place and that may have caused the differences with respect to other biochar from original biomass.

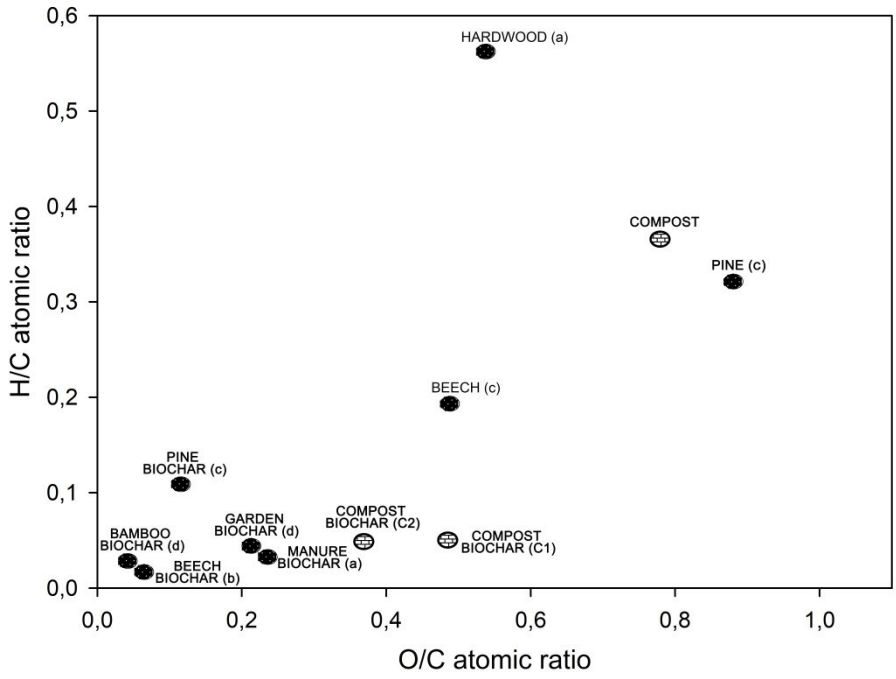

Figure 3. Van Kreveren graph (H/C vs O/C atomic ratio) for the obtained compost biochar with respect to other raw materials ([a]Fabbri et al. (2012); [b]Morin et al. (2016); [c]Guizani et al. (2017); [d]Dang et al. (2021).

Low values of gross heating, 14.18 and 18.56 MJ kg^{-1} for C1 and C2 samples, respectively, have been found. Values similar to 25-30 MJ kg^{-1} in biochars from

different feedstocks have been found (Jiang et al., 2018; Tsai et al., 2018), but higher than those found by Mierzwa-Hersztek et al. (2019), in the range of 11-12 MJ kg^{-1} for sawdust, wheat straw, and miscanthus straw. In this regard, Tripathi et al. (2016) showed that the calorific value of biochar is directly proportional to the process temperature and inversely proportional to the H/C and O/C molar ratios. The obtained data supports the conclusions drawn by these authors.

Alkalinity is one of the most influential properties of biochar, because changes in pH have large impact on many soil processes (Fidel et al., 2017). In this study, values of 12.04 and 12.37 have been found for C1 and C2, respectively. In this regard, Li et al. (2013) and Fidel et al. (2017) showed values between 5.5-10.3 depending on the biochar feedstock and pyrolysis conditions. The values found in biochar from MSW compost, are higher than those found by the previous authors. This fact may be due to the high amount of basic salts usually found in MSW compost (Xie et al., 2020) that give rise to a basic pH already in the original compost and that are concentrated by the pyrolysis process in the biochar obtained since the process conditions (450ºC) do not cause the volatilization of these salts.

3.5. Bio-oil GC/MS analysis

The bio-oil obtained from the pyrolysis of compost at 450 °C for 30 min in a fluidized bed reactor was analyzed by GC-MS and are shown in Table 4. Since the compost is formed mainly by lignocellulosic material composed of cellulose, hemicellulose and lignin, the pyrolysis products are derived from these components in different proportions. Numerous chemical compounds have been obtained in bio-oils but the complete identification is complex, with 24 of the most important compounds identified and studied in depth.

The main cellulose decomposition compound in compost pyrolysis as furan-2-ylmethanol (3.3%) and as nitrogenous product is found 5-(hydroxymethyl)-1-methylpyrrolidin-2-one (2.4%) have been found. As shown in Table 4, the phenolic compounds typical in lignin disintegration, such as methylphenols (12.7%), 2-methoxyphenol, better known as guaiacol (6.9%), 4-methylbenzene-1,2-diol (5.7%) or 3-(2-hydroxyethyl)phenol (6.4%) have been found among many others, assuming more than 80% of the total of degraded products.

The low concentration of short-chain compounds common of the fragmentation of cellulose and hemicellulose such as carbohydrates highlighting the levoglucosan in the pyrolytic liquids (Kim et al., 2013) compared to untreated lignocellulosic biomass reveals the decomposition of these components in the composting process, making more complex lignin compounds attract attention to a greater extent.

Compounds	**Formula**	**MS**	**RT (min)**	**Area (%)**
Ethane-1,2-diol	$C_2H_6O_2$	62.07	12.591	2.45
Furan-2-ylmethanol	$C_5H_6O_2$	98.10	12.904	3.29
Phenol	C_6H_6O	94.11	14.288	6.32
5-(hydroxymethyl)-1-methylpyrrolidin-2-one	$C_6H_{11}NO_2$	129.16	15.653	2.44
2-methylphenol	C_7H_8O	108.14	16.050	3.30
3-methylphenol	C_7H_8O	108.14	16.220	4.58
4-methylphenol	C_7H_8O	108.14	16.444	4.82
3-methylcyclohex-1-en-1-ol	$C_7H_{12}O$	112.17	17.558	6.19
2-methoxyphenol	$C_7H_8O_2$	124.14	18.088	6.29
3-ethylphenol	$C_8H_{10}O$	122.16	18.272	2.11
benzene-1,3,5-triol	$C_6H_6O_3$	126.11	19.040	3.08
2-methoxy-5-methylphenol	$C_8H_{10}O_2$	138.16	19.862	3.34
benzene-1,4-diol	$C_6H_6O_2$	110.11	19.938	3.73
3-methylbenzene-1,2-diol	$C_7H_8O_2$	124.12	21.265	2.68
methyl 3-hydroxybenzoate	$C_8H_8O_3$	152.15	21.321	5.36
2,6-dimethoxyphenol	$C_8H_{10}O_3$	154.16	21.450	3.26

4-methylbenzene-1,2-diol	$C_7H_8O_2$	124.14	21.528	5.69
1-(2-hydroxyphenyl)propan-1-one	$C_9H_{10}O_2$	150.17	22.122	5.06
3-(2-hydroxyethyl)phenol	$C_8H_{10}O_2$	138.16	22.528	6.39
2-methoxy-4-propylphenol	$C_{10}H_{14}O_2$	166.22	22.685	4.62
1-(2-hydroxy-6-methoxyphenyl)ethanone	$C_9H_{10}O_3$	166.17	23.553	4.67
2-methoxy-4-prop-2-enylphenol	$C_{10}H_{12}O_2$	164.20	23.861	2.15
1-(4-hydroxy-3-methoxyphenyl)ethanone	$C_9H_{10}O_3$	166.17	24.359	6.01
4-(3-hydroxypropyl)-2-methoxyphenol	$C_{10}H_{14}O_3$	182.22	28.106	2.15

Table 4. Main compounds found by GC/MS in bio-oil of MSW compost pyrolysis at 450ºC.

3.6. Non-condensable gases GC/MS analysis

The volatile organic pyrolysis products that are found in a small proportion mixed with mainly nitrogen and other light gases detected by GC/MS are shown in Table 5. In this case, the non-condensable gases contain compounds derived from hemicellulose and cellulose, among other compounds of composted urban waste that barely appeared in pyrolytic liquids.

Compounds	Formula	MS	RT (min)	Area (%)
2-methylpropan-1-ol	$C_4H_{10}O$	74.12	4.140	5.27
1-pentanol	$C_5H_{12}O$	88.15	4.255	4.69
pent-1-en-3-yne	C_5H_6	66.10	4.320	2.93
2-methylpropanal	C_4H_8O	72.11	4.425	3.40
hexanal	$C_6H_{11}O$	100.16	4.660	5.04
2,2-dimethylpropanenitrile	C_5H_9N	83.13	4.965	3.37
(3E)-hexa-1,3,5-triene	C_6H_8	80.13	5.195	5.25
4-methylpenta-1,3-diene	C_6H_{10}	82.14	5.315	3.60
hexa-1,5-diyne	C_6H_6	78.11	5.470	3.82
(3E)-hexa-3,5-dien-2-ol	$C_6H_{10}O$	98.14	5.565	4.04
2,2-dimethylpropanal	$C_5H_{10}O$	86.13	5.935	5.48
2-methylpent-4-en-1-ol	$C_6H_{12}O$	100.16	5.990	2.60
2,5-dimethylfuran	C_6H_8O	96.13	6.130	4.45

(5E)-hepta-1,5-diene	C_7H_{12}	96.17	6.510	3.75
ethenyl acetate	$C_4H_6O_2$	86.09	6.665	4.80
5-methylhexa-1,4-diene	C_7H_{12}	96,17	6.985	5.18
(3E)-2-methylhexa-1,3,5-triene	C_7H_{10}	94.15	7.115	4.64
3-prop-2-enylcyclopentene	C_8H_{12}	108.18	7.270	5.25
(5E)-hepta-1,5-dien-3-yne	C_7H_8	92.14	7.755	4.98
cyclopentanone	C_5H_8O	84.12	8.340	4.35
octane	C_8H_{18}	114.23	8.595	3.59
methyl 2-methylpropyl carbonate	$C_6H_{12}O_3$	132.16	10.545	2.75
1,3-xylene	C_8H_{10}	106.16	10.715	3.29
1,2-xylene	C_8H_{10}	106.16	10.965	3.47

Table 5. Main compounds found by GC/MS in non-condensable gases of MSW compost pyrolysis at 450ºC.

A significant amount of alcohols (16.6%) is found in organic gases, such as 2-methylpropan-1-ol (5.3%), 1-pentanol (4.7%), (3E)-hexa-3,5-dien-2-ol (4.0%) or 2-methylpentent-4-en-1-ol (2.6%). There is also a wide variety of aldehydes (13.9%) such as 2-methylpropanal (3.4%), hexanal (5.0%) or 2,2-dimethylpropanal (5.5%). Some compounds derived from hemicellulose and cellulose are also observed, mainly 2,5-dimethylfuran (4.5%). The same compound was also found by Hubble and Goldfarb (2021) in hemicelluloses pyrolytic degradation. A group of compounds derived from plastics and other compounds of more specific urban solid waste can be distinguished, as in the case of 1,3-xylene and 1,2-xylene (3.3% and 3.5%, respectively).

It should be noted that numerous organic compounds with double and triple bonds (36.6%) are obtained from the degradation of carbohydrates, proteins and other typical components of organic matter of animal or human origin (Somorin et al., 2020). The compost has been produced from solid urban waste from

coastal area and is made up of various remains of seashells and bones, so these chemical compounds from its decomposition are common.

4. Conclusions

The behaviour of MSW compost and products formed in fluidized bed pilot plant is similar to that established on lignocellulosics raw material. Four characteristic zones (humidity evolution, hemicellulose decomposition, lignin and cellulose degradation and lignin disintegration) have been found.

The TGA evolution and its kinetic constants similar to those found for lignocellulosic materials have been measured. However, the produced biochar has low stability and aromaticity due to its high and low O/C and H/C ratios, respectively. Additionally, the compounds found in the bio-oil as highly phenolics can be described, it could be due to its humic and fulvic compounds (heavy compounds) in the original material (compost) as well as lignin not degraded during the composting process. Moreover, the compounds in non-condensable gases to thermal degradation of shorter structures such as hemicellulose, proteins and cellulose may be due.

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