

CO-PYROLYSIS OF SEWAGE SLUDGE AND MANURE

Nadia Ruiz-Gómez (nadiarui@unizar.es)^a, Violeta Quispe (vquispe@unizar.es)^a, Javier Ábrego (abrego@unizar.es)^a, María Atienza-Martínez (atienza@unizar.es)^{a,*}, María Benita Murillo (murillo@unizar.es)^a, Gloria Gea (glogea@unizar.es)^a

^aThermochemical Processes Group (GPT), Aragon Institute for Engineering Research (I3A), Universidad Zaragoza, Spain

*Corresponding author:

Phone: + 34876555483 Fax: +34976762043

E-mail: atienza@unizar.es

ABSTRACT

1 The management and valorization of residual organic matter, such as sewage sludge
2 and manure, is gaining interest because of the increasing volume of these residues, their
3 localized generation and the related problems. The anaerobic digestion of mixtures of
4 sewage sludge and manure could be performed due to the similarities between both
5 residues. The purpose of this study is to evaluate the feasibility of the co-pyrolysis of
6 sewage sludge (SS) and digested manure (DM) as a potential management technology for
7 these residues. Pyrolysis of a sewage sludge/manure blend (50:50%) was performed at
8 525 °C in a stirred batch reactor under N₂ atmosphere. The product yields and some
9 characteristics of the product were analyzed and compared to the results obtained in the
10 pyrolysis of pure residues. Potential synergetic and antagonist effects during the co-
11 pyrolysis process were evaluated. Although sewage sludge and manure seem similar in
12 nature, there are differences in their pyrolysis product properties and distribution due to
13 their distinct ash and organic matter composition. For the co-pyrolysis of SS and DM, the

product yields did not show noticeable synergistic effects with the exception of the yields of organic compounds, being slightly higher than the predicted average, and the H₂ yield, being lower than expected. Co-pyrolysis of SS and DM could be a feasible management alternative for these residues in locations where both residues are generated, since the benefits and the drawbacks of the co-pyrolysis are similar to those of the pyrolysis of each residue.

KEYWORDS: sewage sludge; manure; co-pyrolysis; stirred batch reactor.

1. INTRODUCTION

The management and valorization of residual organic matter is a subject of growing interest because of the increasing volume of these residues, their localized generation and the associated environmental, economic and social issues. Sewage sludge and manure are two of the most abundant residues of this kind in Spain. The annual production of sewage sludge and livestock manure was 2.6 and 6 Mt (on a dry basis), respectively, in recent years in Spain (Eurostat, 2014). The residues are similar in nature, in terms of high water and nutrient (N and P) content. For this reason, one of the traditional disposal methods for both residues is land application. However, this practice is limited by environmental regulations and transportation costs. The improper application of these residues to fields, especially in those regions with high concentrations of intensive livestock production, provokes surface and groundwater pollution, odor and air emissions (ammonia and greenhouse gases), and the accumulation of heavy metals in soils. In the specific region of Aragón in Spain, only its capital is densely populated (Zaragoza, around 700,000 inhabitants). Rural areas around it are scarcely populated but some of them have a flourishing farming sector. As a result, around 82 kt/year of sewage sludge are generated, most of them in the area of Zaragoza. On the other hand, more than 11.5 and 2.3 Mt/year of pig and cattle manure are generated in Aragón. This quantity largely

exceeds the local demand for agricultural fertilizers (in terms of N content). Thus, at least a portion of these residues could be co-processed together with sewage sludge. This possibility is encouraged by the Integrated Waste Management Plan of Aragón (GIRA), which aims to achieve a better valorization of the residue flows within the region, while enabling the optimum operation of existing and new treatment plants. Moreover, integrated approaches are demanded for the valorization of residual organic matter such as sewage sludge, manure and/or municipal solid wastes. Therefore, the development of alternative technologies for the management of these kinds of residues is required. In this regard, the pyrolysis of anaerobically digested organic-based wastes appears as a potential method for valorizing these residues. This process stabilizes them, reduces their volume, and produces three product fractions (solid, liquid and gas) valuable for energy and/or chemical production.

The EU Framework Programme for Research and Innovation establishes the need for seeking innovative and sustainable technologies for the management of manure and other effluents from livestock production. A similar approach is applied to sewage sludge. The pyrolysis of each one of these residues has been investigated in the past; for instance, the pyrolysis of sewage sludge has been widely studied for liquid production (Fonts et al., 2012) and also for obtaining solid products that can be used as adsorbents (Smith et al., 2009). Most of the works on liquid obtained from sewage sludge pyrolysis have been focused on its application as a fuel, but its high nitrogen content hinders this usage. For this reason, more recently the use of sewage sludge pyrolysis liquid as a source of valuable chemicals has been investigated (Fonts et al., 2016). Regarding manure pyrolysis, most research works have been devoted to producing biochar for its application as a soil conditioner, showing several benefits as an organic amendment (Meng et al., 2013; Subedi et al., 2016). Studies on manure pyrolysis to produce bio-oil have been

sparse (Cao et al., 2011; Jeong et al., 2015) and mainly focused on poultry manure (Agblevor et al., 2010; Das et al., 2009), showing, as in the case of the bio-oil from sewage sludge, a relatively high nitrogen content compared to lignocellulosic biomass bio-oils.

Other authors have evaluated the co-pyrolysis of sewage sludge and lignocellulosic biomass in order to enhance the properties of the liquid for use as a fuel (Alvarez et al., 2015; Samanya et al., 2012) and to reduce the heat demand of the pyrolysis process (Ding and Jiang, 2013), proposing this co-pyrolysis as a viable solution for the valorization of sewage sludge (Alvarez et al., 2015) without external energy input (Ding and Jiang, 2013). The co-pyrolysis of manure with lignocellulosic biomass (Troy et al., 2013) and with agricultural plastic wastes (Ro et al., 2014) has also been evaluated with the aim of decreasing the energy requirements in the manure pyrolysis process without affecting the biochar properties.

Due to the similarities between sewage sludge and manure, the anaerobic digestion of their mixtures could be performed in locations where both residues are generated locally. Therefore, it would seem desirable to assess the co-pyrolysis of digested sewage sludge and manure with the aim of evaluating the feasibility of their joint valorization. However, the co-pyrolysis of both residues and its potential benefits has been scarcely studied (Sanchez et al., 2007). Sánchez et al. carried out a pilot-scale pyrolysis process for the treatment of a mixture of sewage sludge and cattle manure to evaluate the energetic valorization of the co-pyrolysis products, concluding that the co-pyrolysis products can be used as a fuel provided that the combustion gases are treated (Sanchez et al., 2007). In order to study the technical feasibility of co-pyrolizing these residues it would be necessary to assess the possible antagonist or the synergetic effects of the mixture of sewage sludge and manure on the pyrolysis product properties. However, these effects have barely been analyzed. Furthermore, it would be also interesting to assess the

economic feasibility of this process (Brown et al., 2013; Wright et al., 2010).

The purpose of this study is to compare the main properties of the pyrolysis products obtained from digested sewage sludge (SS) and digested manure (DM) and to ascertain the potential synergetic and antagonist effects during the co-pyrolysis process.

2. MATERIALS AND METHODS

2.1 Materials.

The anaerobically digested and thermally dried SS used for this work was supplied by an urban wastewater treatment plant located in Madrid (Spain). The DM was supplied by the HTN Biogas Company located in Navarra (Spain) and was obtained by anaerobic co-digestion of cattle manure with food and agro-industry wastes. The anaerobically digested manure was separated in a decanter centrifuge and the solid fraction was dried at 105 °C. The proximate and ultimate analysis, the higher heating value, the density and pH of these materials contents are displayed in Table 1. The extractive content of both materials, also shown in Table 1, was determined by Soxhlet extraction with dichloromethane. The content of other organic macromolecules in SS and DM are also displayed in Table 1.

104 **Table 1.** Properties of the materials (wet basis).

Properties	Analytical standard	SS	DM
Ultimate analysis (wt. %)			
Carbon ^a		27.9	31.7
Hydrogen ^{a,b}		4.7	4.2
Nitrogen ^a		4.5	1.9
Sulfur ^a		1.4	0.5
Oxygen ^c		34.6	50.7
Proximate analysis (wt. %)			
Dry matter	ISO-589-1981	93	87
Ash	ISO-18122-2015	40	20
Volatiles	ISO-5623-1974	50	54
Fixed carbon ^d		3	13
Others			
HHV ^e (MJ·kg ⁻¹)	ISO-1928-2009	12.5	13.9
Density ^f (kg·m ⁻³)		0.87	0.26
pH ^g		7.3	8.3
Extractives (wt. %)		3.5	1.0
Protein (wt. %)	EN-13342:2001	28	12
Neutral detergent fiber (NDF) (wt. %)	XP U44-162	26.78	49.54
Acid detergent fiber (ADF) (wt. %)	XP U44-162	4.26	46.77
Lignin (wt. %)	XP U44-162	0.03	16.34
NDF-ADF ^h (wt. %)		22.52	2.77

ADF-Lignin ⁱ (wt. %)		4.23	30.43
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^aUltimate analysis was performed using Carlo Erba 1108. ^bThe wt.% of hydrogen includes hydrogen from the moisture. ^cOxygen (% wt) = 100-Carbon (%)-Hydrogen (%)-Nitrogen (%)-Sulfur (%)-other elements contained in the ash (%) (see Table 2). ^dBy difference. ^eHHV was determined using IKA C 2000 Basic Calorimeter. ^fA known volume of material (25 mL) was weighed and the density was calculated. ^g1 g of solid is stirred for 1.5 h in demineralised water. ^hThis fraction includes components such as hemicellulose. ⁱThis fraction includes components such as cellulose.

Compared to lignocellulosic biomass wastes, SS and DM have higher ash, nitrogen and sulfur contents. The lower ash content of DM (half of that from SS) explains the higher higher heating value (HHV) of this type of residue. The higher oxygen content for DM is not only due to its higher moisture content, but also to its organic chemical composition. This higher oxygen content justifies the lower HHV (if expressed in dry ash free basis) of DM than that of SS (20 vs. 23 MJ·kg⁻¹). Another difference between both raw materials lies in their density, this being much lower for DM. Finally, the extractive and protein content was higher in SS than in DM. The extractives are the most non-polar compounds. The composition of the extractives was analyzed by Gas Chromatography and Mass Spectrometry (GC-MS). The compounds found in the extractives from SS were mainly fatty acids, toluene, benzene derivatives and steroids. The extractive compounds from DM were also fatty acids, toluene and phenolic compounds. DM contains larger amounts of lignin.

The high ash content in both materials could affect the pyrolysis process, since ash has been shown to have some catalytic effects (Aznar et al., 2007). The inorganic compounds found in the ash could increase the yield of char and non-condensable gases (NCG), and decrease the yield of liquid (Sekiguchi and Shafizadeh, 1984). According to Nik-Azar et al. (1997) Na and K have stronger catalytic effect than calcium. Table 2 displays the metal content of the wastes determined by Inductively Coupled Plasma-Atomic Emission

Spectroscopy (ICP-AES).

As can be seen in Table 2, calcium and iron are the most abundant metals in DM and SS ash, respectively.

Table 2. Metal content of SS and DM.

Element	SS (g·kg ⁻¹)	DM (g·kg ⁻¹)
Al	21.75	9.04
As	<0.035	<0.035
Ba	0.333	0.024
Ca	22.99	55.4
Cd	<0.004	<0.004
Co	<0.007	<0.007
Cr	0.080	<0.065
Cu	0.41	<0.034
Fe	66.80	7.86
K	5.03	8.64
Mg	6.81	8.09
Mn	0.25	0.30
Mo	<0.165	<0.165
Ni	<0.021	<0.021
P	30.81	15.16
Pb	0.183	<0.133
Ti	1.5	<0.023
Zn	<0.026	0.33
Hg	<0.026	<0.026
Na	2.33	4.83
Si	48.8	0.39

Figure 1 shows the Fourier transform infrared (FTIR) spectra of both residues.

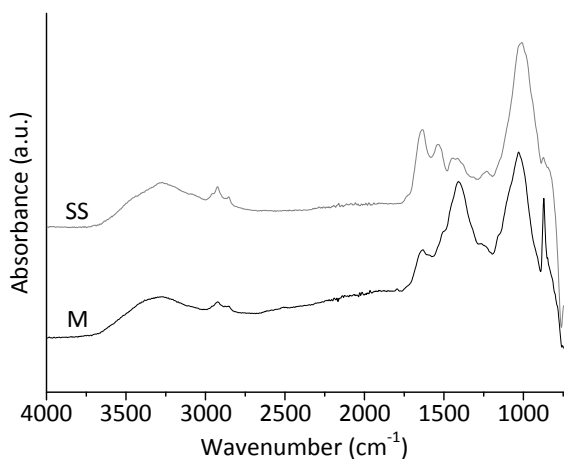


Figure 1. FTIR spectra of SS and DM.

In general, the SS used shows a similar spectrum to others previously reported (Abrego et al., 2009), the main differences (e.g. lower peak intensities) being attributable to the effect of the anaerobic digestion, which greatly reduces the intensity of some bands (Cuetos et al., 2013). The DM used in this work was also anaerobically digested and thus also exhibits broad bands with lower intensities. The comparison between both materials shows some similarities and several differences. Both of them show a band in the 1200-1000 cm^{-1} range attributed to polysaccharides. However, DM shows a distinctive band centered at 1409 cm^{-1} that could be explained by C=O stretching and OH deformation from carboxylic acids (Socrates, 2004). The presence of a higher number of these functional groups in DM could partly explain the higher O content of this material. On the other hand, the bands related to compounds with a protein origin (1790–1500 cm^{-1}) (Cuetos et al., 2013) are much more intense in the case of SS, which is in accordance with the higher N content of this material. The peak at 2800-3000 cm^{-1} indicates the presence of aromatic and aliphatic structures. The broad band between 3000-3700 cm^{-1} corresponds to the O-H stretching in water, alcohols, phenols and carboxylic acids, as well as N-H stretching from amides and amines (Alvarez et al., 2015). Finally, the very

high calcium content in DM could be evidenced by the sharp peak appearing in its spectrum at around 875 cm^{-1} , corresponding to calcium carbonate (Abrego et al., 2009). Another characteristic band for this compound appears at around 1420 cm^{-1} and could contribute to the previously mentioned band found at 1409 cm^{-1} .

As detailed in the next Section, both materials were pyrolyzed in the pyrolysis reactor without prior grinding. The particle size distributions for SS and DM are shown in Table 3.

Table 3. Particle size distribution for the raw materials.

Size (mm)	DM (wt. %)	SS (wt. %)
$\Phi > 4$	23	2
$3 < \Phi < 4$	9	54
$2 < \Phi < 3$	17	40
$0.8 < \Phi < 2$	30	2
$\Phi < 0.8$	21	2

2.2. Experimental system and procedure

Thermogravimetric analyses were performed prior to the pyrolysis runs in the stirred batch reactor. Both experimental systems are briefly described below.

2.2.1. Thermogravimetric analysis (TGA)

Thermogravimetric analyses were performed in order to study the thermal degradation behavior of each residue and of the 50:50% blend. A Netzsch STA 449 Jupiter® thermobalance was used. The two materials were ground and sieved to a particle size lower than $50\text{ }\mu\text{m}$. The SS/DM blend (50%:50%) was prepared by blending both wastes, ground and sieved. The operating conditions used were the same for the three samples (SS, DM and SS/DM). The samples (ca. 20 mg) were heated up to $900\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ under N_2 atmosphere (flow rate of $50\text{ mL (STP)}\cdot\text{min}^{-1}$). Two replicates

were performed for each feedstock.

2.2.2. Pyrolysis tests in the stirred batch reactor.

A bench-scale stirred batch reactor was used to pyrolyze each residue alone (SS and DM) and also the 50:50% blend (SS/DM). Figure 2 illustrates the laboratory scale setup. The cylindrical reactor has a diameter of 107 mm and a length of 294 mm. The reactor capacity depends on the bulk density of the solid material fed. Since the bulk density of SS is higher, the amount of sample placed in the reactor was approximately 600 g for SS pyrolysis runs and around 300 g for DM and SS/DM runs. Four K-type thermocouples were used to register the temperature profiles in the reactor. The pyrolysis experiments were performed under N_2 atmosphere ($250 \text{ mL (STP)} \cdot \text{min}^{-1}$) at $525 \text{ }^\circ\text{C}$ as the final temperature and at a heating rate of around $8 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ (this was the maximum heating rate achievable by the experimental system). The final temperature was maintained for 30 min. The vapors produced during the pyrolysis process passed through the condensing zone. The condensable fraction (water and organic compounds) was collected in two ice-cooled condensers and one electrostatic precipitator. The composition of NCG was analyzed by a micro-gas chromatograph (micro-GC) connected online. Specifically, the analyzed gases were CO_2 , CO , H_2 , CH_4 , C_2H_2 , C_2H_4 , C_2H_6 and H_2S . The experiments were conducted in duplicate.

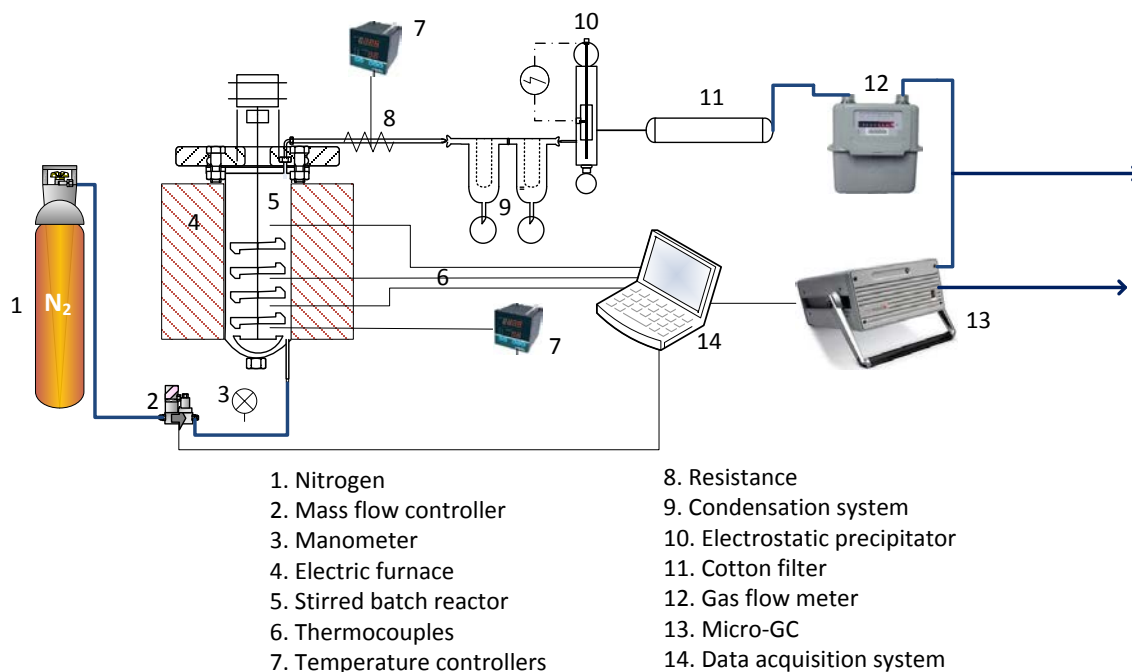


Figure 2. Laboratory scale pyrolysis setup.

2.2.3 Characterization of pyrolysis products

The mass yields of each one of the pyrolysis products (η_{product}) were calculated as the percentage ratio between the mass of pyrolysis product and the mass of feedstock introduced into the reactor. The mass of solid (char) and liquid obtained was determined gravimetrically. The mass of gas obtained was calculated taking into account the gas composition provided by the micro-GC and the known volumetric flow of nitrogen introduced.

The lower heating value of the gas (free of N_2) (LHV_{gas}) was calculated considering the gas composition and the lower heating value of each gas compound. The ultimate and proximate analyses and the higher heating value of the char (HHV_{char}) obtained in each experiment were determined. The FTIR analysis of the char was also performed and the results were compared to the FTIR spectra of the different residues.

The liquid, which separated into two phases (aqueous phase (AP) and organic phase (OP)) in all the experiments performed, was centrifuged at 4500 rpm (2038 x g) for 30 min using a Heraeus Megafuge 16 Centrifuge to separate both phases. The phases were stored in a fridge at between 3 °C and 5 °C until they were analyzed. The water content (WC, mass fraction %) of each phase was determined by the Karl-Fischer titration method. The density of both phases was determined using a portable Mettler Toledo densimeter (model Densito 30 PX). The ultimate analysis and the higher heating value of the organic phase (HHV_{OP}) were also measured. The organic compounds present in both phases were identified and semi-quantified by GC-MS and GC-FID. The chromatographic methods used for both phases showed certain differences. The capillary column used for analyzing the aqueous phases was a 50 m x 200 µm x 0.3 µm HP-FFAP Polyethylene Glycol TP. Helium of 99.999% purity was used as the carrier gas and the injector temperature was set at 300 °C. The temperature program adopted was the following: initial oven temperature at 60 °C held for 6 min followed by an increase to 80 °C at a rate of 1.5 °C·min⁻¹ and held for 5 min, consequently increased to 200 °C at a rate of 1 °C·min⁻¹ and held for 5 min, and finally increased to 240 °C at a rate of 1.8 °C·min⁻¹ where it was held for 30 min. The capillary column used for the organic phases was 60 m x 250 µm x 0.25 µm DB-17ms. The carrier gas and the injector temperature were similar to those used for the aqueous phases. The temperature program was as follows: initial oven temperature at 60 °C held for 5 min followed by an increase to 250 °C at a rate of 1.5 °C min⁻¹ and held for 5 min, and finally an increase to 310 °C at a rate of 2 °C·min⁻¹ and held for 5 min. The analysis procedure used considers all the response factors to be similar. It therefore does not give quantitative results but is suitable for comparing relative percentages of compounds in pyrolysis liquids.

The energy yield of the different products, defined according to equation [1], was

calculated for each run.

$$energy\ yield_i = \frac{\eta_i HHV_i}{HHV} \times 100 \quad [1]$$

where η_i and HHV_i are the mass yield and the higher heating value of each pyrolysis product (gas, organic liquid phase and char, respectively) and HHV is the higher heating value of the material introduced into the reactor (or the average of HHVs in the case of SS/DM).

Finally, the energy requirement for the pyrolysis process was estimated for each waste and the blend. The procedure followed to solve the energy balances was similar to those used by other researchers (Abrego et al., 2013; Atienza-Martinez et al., 2015; Gil-Lalaguna et al., 2014).

3. RESULTS AND DISCUSSION

3.1 TGA experiments

The mass loss (TG) and derivative mass loss (DTG) curves are displayed in Figure 3. Both materials show total mass loss greater than 50% at the final temperature of 900 °C and a main decomposition stage in the temperature interval between 200 and 400 °C. This stage begins slightly later for DM than for SS (DTG peaks at 325 °C and 310 °C, respectively) which could be explained by the higher cellulose content in DM. Immediately after this main decomposition stage, SS shows additional mass loss evidenced by a shoulder in its DTG curve, which can be associated with protein decomposition. The region between 500 and 650 °C is quite similar for both materials, with relatively constant mass loss. Major differences arise at higher temperatures, with more significant mass loss for DM peaking at 715 °C. This peak may be attributed to

calcium carbonate decomposition (Abrego et al., 2009). This compound has been identified in the FTIR spectrum of DM (Figure 1). Furthermore, calcium is the most abundant component of the DM ashes, and the manure pH, higher than 7, indicates a significant proportion of carbonates in the ashes (Schumacher, 2002).

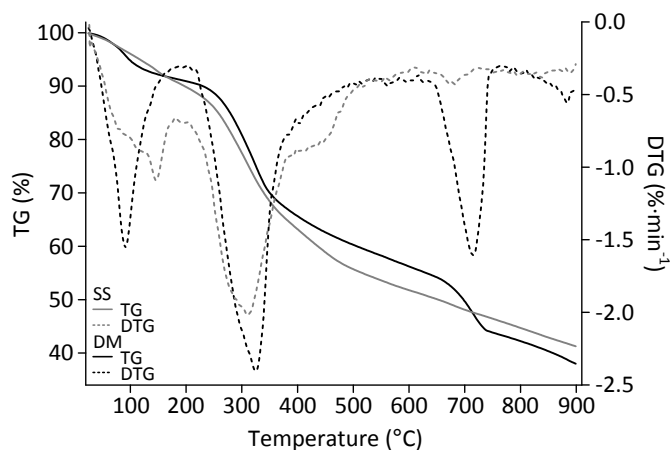


Figure 3. Mass loss (TG) and derivative mass loss (DTG) curves for SS and DM.

The experimental and the predicted (arithmetic average from the results obtained for each material) DTG curves for SS/DM are compared in Figure 4 in order to assess potential synergistic effects. In order to better compare the main decomposition features, the drying region, below 100 °C, is not shown in the figure. The predicted and the experimental curves were quite similar. The region below 500 °C was almost identical, with a minor difference in the DTG peak maximum (the predicted curve showed a DTG peak maximum at 318.5 °C, whereas the experimental curve gave 312.5 °C). At higher temperatures, experimental data showed lower mass loss than predicted, especially from 700 °C. It seems that the carbonate decomposition region already shown for DM in Figure 3 was affected in two ways by the presence of SS. On the one hand, the experimental DTG temperature peak was 698.5 °C vs. the predicted peak at 713.5 °C. On the other hand, the total mass loss in this stage was lower than the arithmetic average of both

contributions.

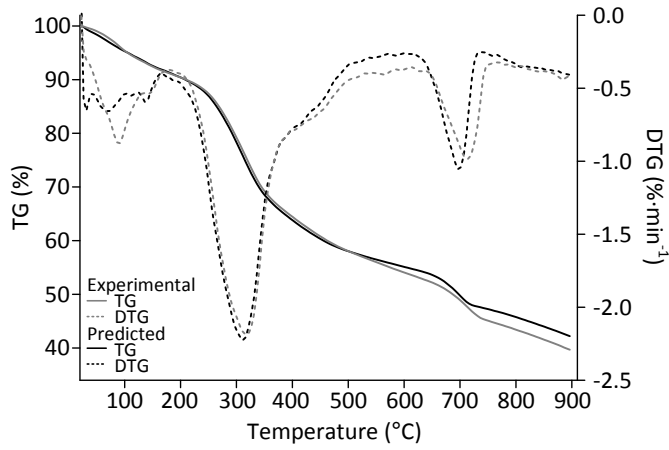
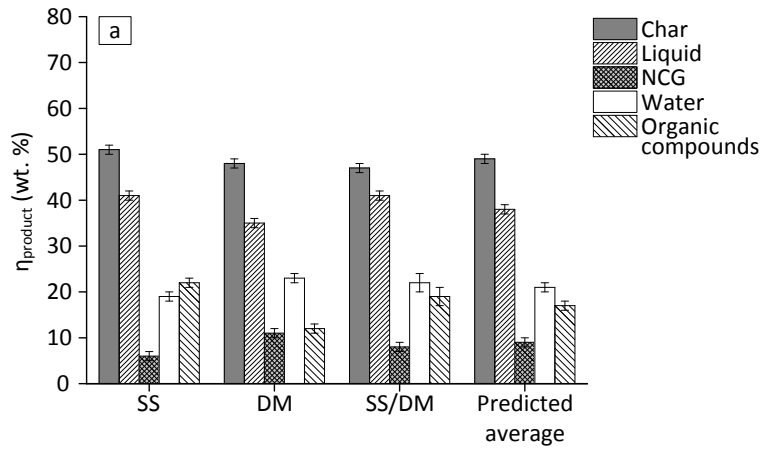


Figure 4. Experimental and predicted TG and DTG curves for SS/DM blend.

3.2 Product yields in the stirred batch reactor

Mass balance closure was higher than 90% for all the experiments performed. Pyrolysis product yields from the pyrolysis of each residue and from the co-pyrolysis of both are displayed in Figure 5. The predicted average yields are also shown in Figure 5.



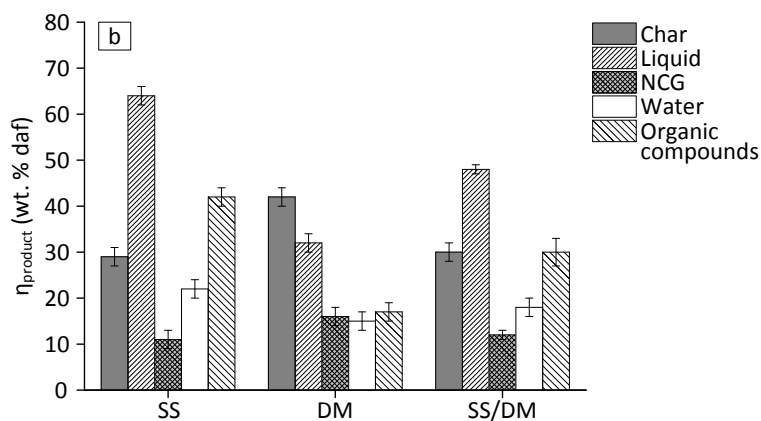


Figure 5. a) Product yields, expressed on feedstock basis, from the pyrolysis of SS, DM and SS/DM b) Product yields, expressed on a dry ash free basis, from the pyrolysis of SS, DM and SS/DM.

Although sewage sludge and manure are not very different in nature, their pyrolysis product distribution showed certain differences. The pyrolysis of DM produced a higher gas yield, and lower char and liquid yields than the pyrolysis of SS (Figure 5a). The higher ash content of SS explains its higher char yield. However, if expressed on a dry ash free basis, the char yield from the DM pyrolysis is higher than that from SS (see Figure 5b). These results are in accordance with the higher fixed carbon content of the DM (see Table 1), which could be justified by its higher lignin content and lower extractives content. It is known that the char yield from the pyrolysis of lignin is high (Qu et al., 2011) whereas the char yield from the pyrolysis of lipids or extractives is low. Sewage sludge contains a higher proportion of proteins and the char from the pyrolysis of proteins is also high (Kebelman et al., 2013), but not as high as that from lignin. The higher gas yield from the pyrolysis of DM could be attributed to the catalytic activity of the metals present in the ash (Manya et al., 2006). DM contains higher concentrations of Ca and Na than SS (5.5% and 0.5% for Ca and Na in DM vs. 2.3% and 0.2%, respectively, in SS). These

species would promote the degradation of the organic matter, favoring the gas formation (Zabeti et al., 2012). The higher moisture content of DM could explain the higher water yield from the pyrolysis of DM. However, the water yield expressed on dry ash free basis was lower using DM as the feedstock (see Figure 5b). The water generated by the pyrolysis reactions was higher in the case of the SS pyrolysis. The higher H/O molar ratio in SS ($H/O = 2.2$ for SS vs. $H/O = 1.1$ for DM, expressed on dry basis) makes it possible that a greater amount of the organic oxygen present in the starting material may be converted into water during the pyrolysis process (Mullen and Boateng, 2011). Other authors have observed that the pyrolysis of biomass with high protein content results in higher water production because of the reaction of nucleophilic amine groups with electrophilic oxygen groups releasing water (Mullen and Boateng, 2011). The DM used in this study has lower protein content than the SS, which could produce lower amounts of pyrolytic water and consequently a lower water yield, expressed on dry ash free basis. The amount of condensable organic compounds generated by pyrolysis was much lower for DM. DM has a lower amount of extractives than SS. Lipids generate a high level of volatiles (Kebelmann et al., 2013) which could explain the higher organic compound yield from SS. Furthermore, the presence of a higher content of some alkali metals such as Ca and Na in DM could also provoke a reduction in the yield of organic compounds, promoting the gas yield (Zabeti et al., 2012).

For the co-pyrolysis of SS and DM, the product yields showed an expected behavior, i.e. there were no noticeable synergistic effects, with the exception of the yield of organic compounds. The product yields obtained from the pyrolysis of the blend of SS and DM was approximately the average of the yields obtained from each individual residue (Figure 5a). However, the yield of organic compounds obtained from the pyrolysis of the SS/DM blend was slightly higher than the predicted average. This might be attributed to

the reduction in the alkali metal content in the SS/DM blend feedstock compared to DM, causing the secondary reactions to occur to a lesser extent. Other authors have observed important synergies in the co-pyrolysis of sewage sludge and different types of lignocellulosic biomass, such as poplar sawdust (Zuo et al., 2014), rice husk (Zhang et al., 2015) and sawdust (Alvarez et al., 2015), which they have attributed to the catalytic activity of the ash present in the sewage sludge. The synergy resulted in increasing gas yields and decreasing bio-oil yields. The more similar ash content in SS and DM in comparison with lignocellulosic biomass could explain the lesser synergistic effect on the product yields between the two materials studied in this work.

3.3. Gas characterization

The yields of NCG obtained from the pyrolysis of each residue and the co-pyrolysis are displayed in Figures 6a and 6b. The major gas compound in all the experiments was CO₂. The pyrolysis of SS produced lower yields of CO₂ and CO and higher yields of H₂ and H₂S than the DM pyrolysis. CO₂ and CO derived from decarboxylation and decarbonylation reactions, respectively. The higher proportion of carbonyl and carboxyl groups in DM enhanced the formation of both CO₂ and CO. Furthermore, Na and Ca, which are present in higher proportions in DM, are active catalysts for generating CO₂ and CO during pyrolysis (Zabeti et al., 2012). The higher molar ratio H/C in SS (1.6 for SS vs. 0.9 for DM, expressed on dry basis), together with the higher content of Al₂O₃ in the SS ashes which might promote H₂ production (Azuara et al., 2013), could explain the higher H₂ yield in the SS pyrolysis. Furthermore, the higher lignin content in DM disfavors H₂ production, since lignin devolatilization generates less H₂ than other chemical constituents, such as cellulose or hemicellulose (Li et al., 2004). The lower H₂S yield from the pyrolysis of DM could be explained by the lower S content in this material.

As can be seen from Figure 6, no relevant synergistic effects regarding the gaseous

products were found when pyrolyzing SS/DM, with the exception of H₂. The yield of H₂ from the co-pyrolysis was lower than that calculated as the predicted average. This antagonist effect might be attributed to the reduction in the Al content in the SS/DM blend feedstock compared to SS.

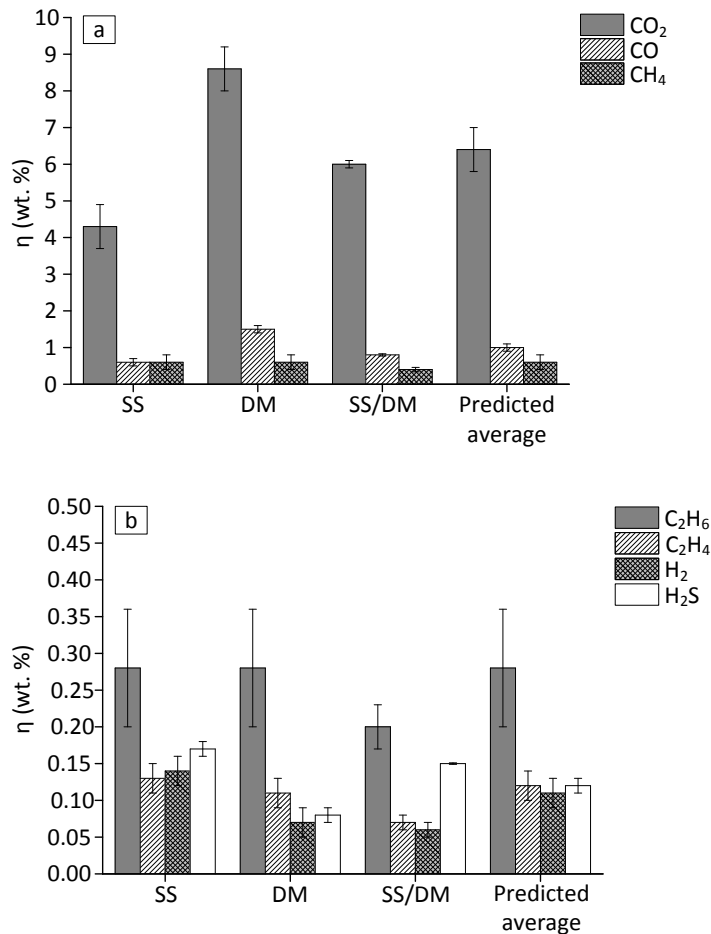


Figure 6. NCG yields from the pyrolysis of SS, DM and SS/DM blend a) CO₂, CO, and CH₄ yields, b) H₂, H₂S, C₂H₄, and C₂H₆ yields.

According to the gas composition, the LHV_{gas} (N₂ free) from the DM pyrolysis ($6 \pm 1 \text{ MJ} \cdot \text{m}^{-3}_{\text{STP}}$) was lower than that from the SS pyrolysis ($10 \pm 1 \text{ MJ} \cdot \text{m}^{-3}_{\text{STP}}$). The LHV_{gas} from the SS/DM co-pyrolysis ($6 \pm 1 \text{ MJ} \cdot \text{m}^{-3}_{\text{STP}}$) was similar to the LHV_{gas} from DM and lower than predicted average value ($8 \pm 1 \text{ MJ} \cdot \text{m}^{-3}_{\text{STP}}$) since, as already indicated, the H₂ yield is also lower. In any case, the LHV of the NCG produced from the three

types of feedstock could be enough to use the gas as a fuel, although a system for cleaning combustion gases would be required.

3.4. Liquid characterization

The liquid product obtained from the pyrolysis of each residue is heterogeneous, showing two different phases (AP and OP, as stated in the Experimental Section). The AP was the major liquid phase in all the runs (Table 4). The OP yield was much lower from the DM than from the SS pyrolysis. However, the AP yield was similar for all the runs (Table 4). The OP yield obtained from the co-pyrolysis seemed to increase slightly more than the amount explainable by a predicted average, as was the case with the yield of organic compounds. Water was the major component present in the liquid. Table 4 shows the water content of the liquid phases obtained. The OP from the DM pyrolysis and from the co-pyrolysis showed a higher water proportion than the OP obtained from the SS pyrolysis. More polar organic compounds can be expected in the OP from the DM pyrolysis.

Table 4. Liquid phase yields (expressed on a feedstock basis) and water content. The values are expressed as mean \pm standard deviation

Feedstock	Liquid phase yields (wt. %)		Water content (wt. %)	
	OP	AP	OP	AP
SS	13 \pm 1	28 \pm 1	7 \pm 2	63 \pm 1
DM	5.5 \pm 0.5	29.8 \pm 0.5	17 \pm 6	75 \pm 1
SS/DM	11 \pm 1	29 \pm 1	15 \pm 5	68 \pm 2
Predicted average	9 \pm 1	29 \pm 1	12 \pm 6	69 \pm 1

As shown in Table 5, the HHV of the organic phases obtained from each residue reflected the potential of these fractions for their use as liquid fuels. However, their nitrogen and sulfur contents, which are relatively high, hinder this application, since their combustion may lead to NO_x and SO_x generation. The N content in the organic phase

390 from the pyrolysis of DM was lower than that of the OP from the pyrolysis of SS because
391 the N content in SS is higher. Nevertheless, the application of these OPs as a source of
392 valuable chemical products, such as N-containing compounds (amides, imidazoles and
393 pyridines, among others), could represent an opportunity for SS and DM, since there are
394 not too many renewable sources for these types of compound (Fonts et al., 2016). No
395 noticeable synergistic effects were reflected for the SS/DM blend in either the ultimate
396 analysis or the H/C and O/C molar ratios.

Table 5. Ultimate analysis (dry basis), molar ratios H/C and O/C (dry basis), and higher heating value of the organic phases (wet basis). The values are expressed as mean \pm standard deviation

	SS	DM	SS/DM	Predicted average
Carbon (wt. %)	69 \pm 1	69 \pm 5	65 \pm 8	69 \pm 5
Hydrogen (wt. %)	9 \pm 0.2	7.2 \pm 0.4	7 \pm 2	8.0 \pm 0.4
Nitrogen (wt. %)	8.3 \pm 0.2	4.9 \pm 0.2	6.9 \pm 0.4	6.6 \pm 0.2
Sulfur (wt. %)	1.9 \pm 0.2	1.4 \pm 0.3	1.9 \pm 0.5	1.7 \pm 0.3
Oxygen (wt. %) ^a	12 \pm 1	18 \pm 5	19 \pm 8	15 \pm 5
H/C	1.6	1.3	1.3	1.4
O/C	0.1	0.2	0.2	0.2
HHV (MJ kg ⁻¹)	34 \pm 2	29 \pm 2	29 \pm 4	32 \pm 2

^aCalculated by difference.

Table 6 shows the ultimate analyses of the aqueous phases and the pH of these phases. As can be observed, the pH of the AP from the DM pyrolysis was lower than that of the SS pyrolysis.

Table 6. Ultimate analysis (dry basis) and pH for the aqueous phases. The values are expressed as mean \pm standard deviation

	SS	DM	SS/DM	Predicted average
Carbon (wt. %)	27 \pm 1	23 \pm 1	24 \pm 1	25 \pm 1
Hydrogen (wt. %)	7.2 \pm 0.3	7.6 \pm 0.2	6.6 \pm 0.4	7.4 \pm 0.2
Nitrogen (wt. %)	16 \pm 1	6 \pm 1	11 \pm 2	11 \pm 1
Sulfur (wt. %)	1.2 \pm 0.1	0.43 \pm 0.05	0.69 \pm 0.03	0.8 \pm 0.1
pH	9.5 \pm 0.5	6 \pm 1	8.7 \pm 0.2	8 \pm 1

3.4.1 Composition of the organic phases

The organic compounds identified by GC-MS in the OP have been grouped into chemical families. The area percentage of each family identified is shown in Figure 7.

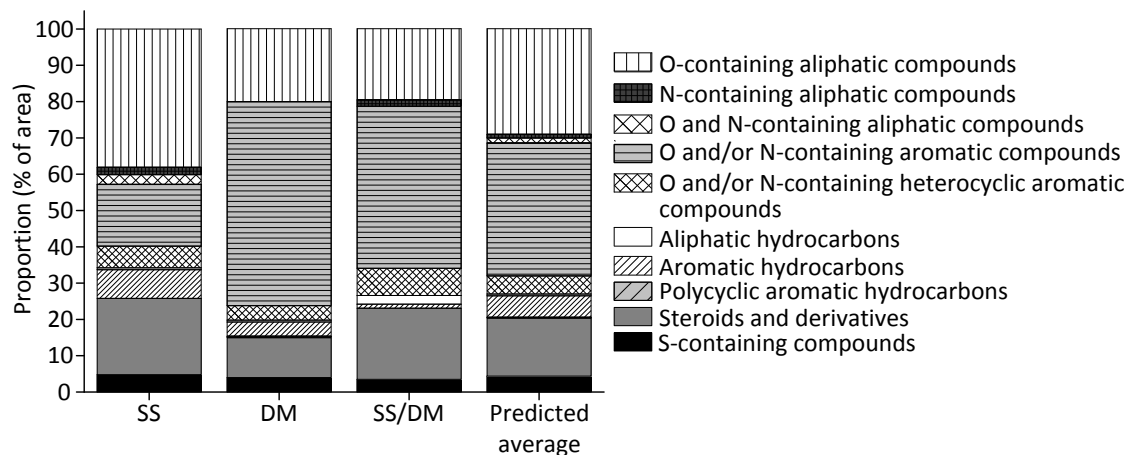


Figure 7. Composition of the OP obtained from the pyrolysis of SS, DM and SS/DM.

Table 7 shows the chromatographic area percentages of certain organic compounds identified in the organic phase obtained in the co-pyrolysis of SS and DM, and of those derived from the pyrolysis of each material independently.

Table 7. Chromatographic area percentage of certain organic compounds identified in the OP obtained from the pyrolysis of SS, DM and SS/DM blend.

	SS (%)	DM (%)	SS/DM (%)
Carboxylic acids	31.8	13.0	10.7
Alcohols	1.3	3.2	2.5
Nitriles	3.2	0.0	2.9
Phenols	10.0	31.9	31.1
Cholestenes	12.2	1.3	8.4

Oxygen-containing aliphatic compounds (mainly carboxylic acids), as well as steroids and their derivatives, were the main compounds in the OP from the pyrolysis of SS. However, the main organic compounds from the pyrolysis of DM were nitrogen and/or oxygen-containing aromatic compounds (mainly phenols). Fatty acids stem from their direct devolatilization from SS and DM, since the extractives of both residues also contain these compounds. The lower extractives content in DM could explain the lower proportion of steroids in the organic phase from DM. The OP from the pyrolysis of DM exhibited a lower proportion of non-polar compounds, which could justify its higher water content. Phenols, more abundant in the OP from the pyrolysis of DM, could come from lignin and protein decomposition. DM is characterized by its lignin and protein content, which could generate phenolic compounds during pyrolysis (especially lignin) (Amen-Chen et al., 2001; Parnaudeau and Dignac, 2007). The greater lignin content of DM could explain the greater proportion of phenols in the OP from the pyrolysis of this residue than in the OP from the pyrolysis of SS. Furthermore, it is noteworthy that no nitrogen-containing aliphatic compounds (such as nitriles) were present in the OP from the pyrolysis of DM. Aliphatic nitriles come from the reaction between fatty acids and ammonia, both produced during pyrolysis. Not enough fatty acids and/or ammonia were

generated during the DM pyrolysis to generate aliphatic nitriles. However, the proportion of fatty acids decreased and the proportion of aliphatic nitriles increased in the OP from the pyrolysis of the SS/DM blend in comparison to the predicted average proportions. This could be provoked by the reaction of the fatty acids from the DM pyrolysis with the ammonia from the SS pyrolysis.

3.4.2. Composition of the aqueous phases

The organic compounds identified in the AP by GC-MS have been grouped into the chemical families whose area percentages are shown in Figure 8.

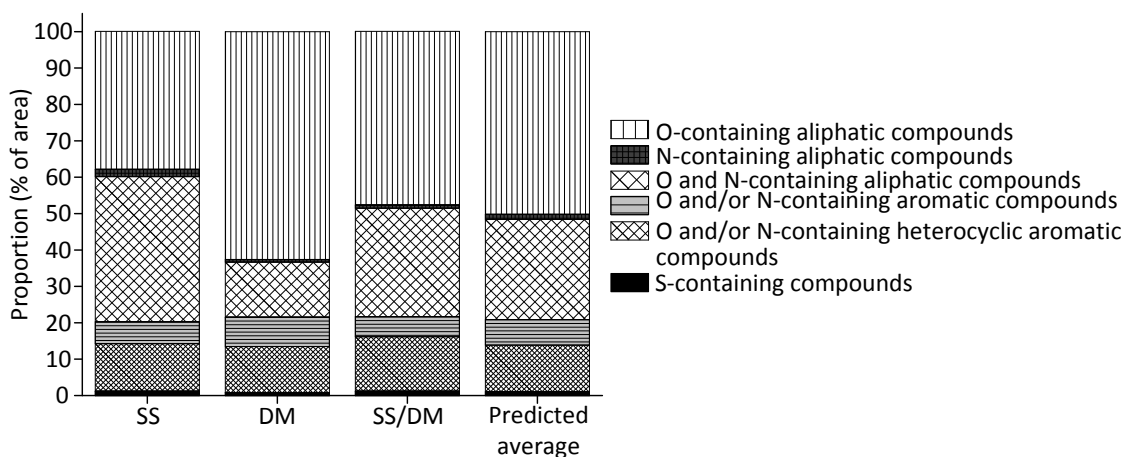


Figure 8. Composition of the AP obtained from the pyrolysis of SS, DM and SS/DM blend.

The area percentages of the different chemical families present in the AP from the pyrolysis of the SS/DM blend were similar to the predicted averages. In this regard, the synergistic effects were less pronounced on the AP than on the OP.

Table 8 shows the chromatographic area percentages of certain organic compounds identified in the aqueous phases.

Table 8. Chromatographic area percentages of certain organic compounds identified in the AP from the pyrolysis of SS, DM and SS/DM blend.

	SS (%)	DM (%)	SS/DM (%)
Carboxylic acids	35.6	34.0	38.9
Alcohols	0.5	6.2	2.1
Ketones	0.4	8.7	1.7
Lactones	0.0	4.7	1.4
Amides	19.0	4.7	13.5
Furans	0.0	4.3	2.2
Pyrroles	9.1	4.1	5.8
Imidazoles	7.5	1.3	7.1
Phenols	1.7	7.5	3.5
Pyridines	7.2	5.3	7.1
Pyrazines	0.0	2.1	3.8

Oxygen and nitrogen-containing aliphatic compounds, mainly amides, and oxygen-containing aliphatic compounds, mainly carboxylic acids, were the most abundant families in the AP from the pyrolysis of SS. In the case of DM, carboxylic acids were by far the major organic compounds. Alcohols, ketones and lactones were also significant in the AP from the pyrolysis of DM, which would come from the devolatilization of cellulose or other polysaccharides in the DM (Parnaudeau and Dignac, 2007). Acetic acid was the organic compound found in the greatest proportion in the AP obtained from each individual residue and from the SS/DM blend, being more abundant in the AP from the pyrolysis of DM. This could explain its lower pH. Acetic acid comes from the elimination of acetyl groups present in polysaccharides (Prins et al., 2006), such as cellulose, which are more abundant in DM than in SS. The higher content in polysaccharides of DM could also explain the higher proportion of furans (Parnaudeau and Dignac, 2007) in the AP from the pyrolysis of this residue than that of SS. Again, the greater proportion of phenols in the AP from the pyrolysis of DM than that of SS could be attributed to the higher lignin content of DM. The total proportion of oxygen and/or nitrogen-containing heterocyclic aromatic compounds, mainly pyridines, pyrazines, pyrroles and imidazoles, was similar

for both materials. Pyridines and pyrazines could come from nucleic acids and amino acids with heteroatomic rings (Fullana et al., 2003). Pyridines, which could come from proteins which contain aniline, were more abundant in the AP from the pyrolysis of SS. Pyrazines, which could also derive from the Maillard reaction which involves the formation of N-heterocycles by amino acids interacting with sugars (Schnitzer et al., 2007), were only present in the AP from DM. The higher proportion of pyrroles (Tsuge and Matsubara, 1985) and imidazoles in the AP from the pyrolysis of SS was also related to the higher protein content in this residue compared to DM. Acetamide, which could come from the pyrolysis of labile proteins that contain glycine (Parnaudeau and Dignac, 2007; Zhang et al., 2013) or from cell wall amino sugars (Eudy et al., 1985), was present in a higher proportion in the AP from the pyrolysis of SS, due to the higher content of proteins in SS. This could contribute to the increase of the pH of the AP from the SS pyrolysis.

3.5. Char characterization

The properties of the chars obtained from the different pyrolysis runs are summarized in Table 9.

Table 9. Properties of the chars obtained from the pyrolysis of SS, DM and SS/DM blend.

The values are expressed as mean \pm standard deviation

Properties	SS	DM	SS/DM	Predicted average
Ultimate analysis (wt. %)				
Carbon	20 ± 2	42 ± 2	30 ± 0.4	31 ± 2
Nitrogen	2.5 ± 0.1	1.8 ± 0.1	2.38 ± 0.03	2.2 ± 0.1
Hydrogen	0.94 ± 0.06	1.51 ± 0.04	1.18 ± 0.08	1.23 ± 0.06
Sulfur	1.3 ± 0.1	0.89 ± 0.01	0.9 ± 0.2	1.1 ± 0.1
Proximate analysis (wt. %)				
Volatile matter	20.2 ± 0.5	20.2 ± 0.9	19.5 ± 0.1	20.2 ± 0.9
Fixed carbon	5.7 ± 0.5	37 ± 1	18.2 ± 0.4	21 ± 1
Ash	74 ± 1	42 ± 1	62.2 ± 0.3	58 ± 1
HHV (MJ·kg⁻¹)	8 ± 1	14 ± 2	11 ± 1	10 ± 3

The char obtained from the DM pyrolysis exhibited, in principle, better characteristics for energetic applications than that from the SS pyrolysis: the ash content was lower and the fixed carbon content was higher in the DM char than in the SS char, which led to a higher calorific value in the former. Furthermore, the content of nitrogen and sulfur, which act as contaminants in a fuel, were lower in the DM char. Nevertheless, the ash, nitrogen and sulfur contents of the DM char were still high in comparison with chars from other types of biomass, such as lignocellulosic ones. The char obtained from SS/DM co-pyrolysis shows no significant interactions between SS and DM. The uses of the char

obtained from the co-pyrolysis could be similar to those proposed for the char from the pyrolysis of each individual residue, such as adsorbent solids and soil amendments. However, the potential application of the char as soil amendment should be corroborated from an agronomic point of view.

Figure 9 shows the FTIR results from the char obtained from the pyrolysis of DM, SS and SS/DM blend.

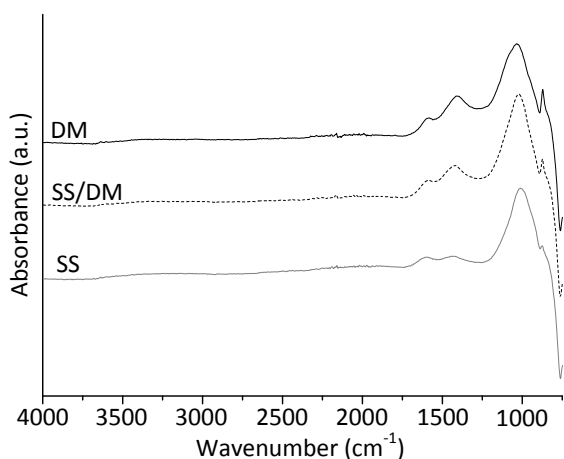


Figure 9. FTIR spectra of SS, DM and SS/DM chars.

A comparison with the FTIR spectra of the starting materials (shown in Figure 1) shows that pyrolysis causes the reduction or even disappearance of most of the previously identified peak regions. This can be correlated with some of the findings reported in the sections describing the composition of the OP and AP liquid fractions. In particular, the abundance of N-containing compounds, alcohols, phenols and fatty acids in the liquids might account for the absence of the previously identified N-H and O-H stretching (3000-3700 cm⁻¹) and protein band (1500-1790 cm⁻¹), whereas the reduction of the C=O stretching (1409 cm⁻¹) in the case of DM could lead to the formation of oxygenated compounds such as ketones, abundant in the AP from this material. SS/DM chars still

519 show the presence of calcium carbonate inherited from DM.

520 3.6. Energy analysis

521 The energy yields of the products, based on HHV, indicate the percentage of the initial
522 energy content of the residue contained in each pyrolysis product. Table 10 displays the
523 energy yield results.

Table 10. Energy yields of the products. The values are expressed as mean \pm standard deviation

	SS (%)	DM (%)	SS/DM (%)	Predicted average (%)
NCG	6 ± 1	6 ± 2	4 ± 1	6 ± 2
OP	35 ± 2	12 ± 2	24 ± 2	23 ± 2
Char	33 ± 1	49 ± 5	40 ± 1	41 ± 5
Total	74 ± 2	67 ± 5	68 ± 2	70 ± 5

The total energy yield in the case of the SS pyrolysis was higher than that obtained for the pyrolysis of DM, mainly due to the lower energy recovery of the OP.

The energy balances were calculated for the system shown in Figure 10 to compare the energy requirements for the pyrolysis of each individual residue and for the SS/DM blend.

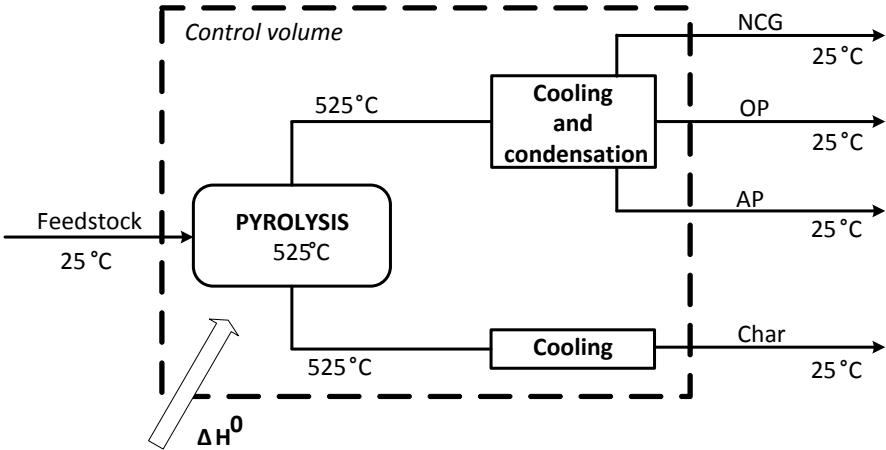


Figure 10. Energy balance system for pyrolysis of SS, DM and SS/DM. Reference temperature: 25 °C. Reference pressure: $1.01 \cdot 10^5$ Pa.

The different feedstocks and the pyrolysis products have been considered to be at the reference conditions of pressure and temperature (25 °C and $1.01 \cdot 10^5$ Pa). This means

that the energy released from the cooling of the char and the NCG, and from the cooling and the condensation of the condensable vapors, was completely used. Assuming no heat losses in the system, the input energy (H_{input}) included the feedstock chemical energy. The output energy (H_{output}) included the chemical energy of all the products. The chemical energy of the feedstocks, the char and the OP has been calculated from their ultimate analyses and their HHVs. In the case of the AP, the chemical energy has been determined assuming that these phases were a blend of water and acetic acid, which was the most abundant organic component in the aqueous phases.

Taking into account the aforementioned simplifications, the ΔH^0 , calculated using equation [2], indicates the energy requirement of the process (per kg of feedstock).

$$\Delta H^0 = H_{output} - H_{input} = \frac{\sum_i \eta_i \cdot \Delta H_{f,i}^0}{100} - \Delta H_{f,feedstock}^0 \quad [2]$$

where η_i is the yield of each product, $\Delta H_{f,i}^0$ the apparent enthalpy of formation of each product and $\Delta H_{f,feedstock}^0$ the apparent enthalpy of formation of the feedstock.

The ΔH^0 has been calculated for each one of the pyrolysis runs. The results are presented in Table 11.

Table 11. ΔH^0 obtained for pyrolysis of SS, DM and SS/DM. The values are expressed as mean \pm standard deviation

	ΔH^0 (MJ·kg ⁻¹)
SS	-0.6 \pm 0.1
DM	-4.2 \pm 0.8
SS/DM	-2.1 \pm 0.1
Predicted average	-2.4 \pm 0.1

All the values obtained for ΔH^0 were negative which theoretically means that in the absence of heat losses, the energy that could be used from the cooling and condensation

of the products was higher than the energy required for the process. In these terms, the DM pyrolysis and co-pyrolysis of both residues showed much more exothermic behavior than the SS pyrolysis.

However, the energy required for the drying of both residues should also be considered. The heat required to reduce the water content of the residues from 65% (typical minimum humidity value obtained from a mechanical dehydration system) to 7-10%, which is recommended for the pyrolysis process, was approximately $4 \text{ MJ} \cdot \text{kg}^{-1}$ of dried residue (Gil-Lalaguna et al., 2014). Therefore, it is important to efficiently use the energy for the cooling and condensation of the pyrolysis products from an energetic point of view.

4. CONCLUSIONS

The co-pyrolysis of sewage sludge (SS) and digested manure (DM) has been investigated. The char yield from the pyrolysis of DM (dry ash free basis) was higher than that from SS, which is consistent with its higher lignin and lower extractive contents. The pyrolysis of SS produced a gas with higher LHV, but the DM char exhibited better characteristics for energetic applications. The organic compounds and water yields (dry ash free basis) were larger in the pyrolysis of SS, which could be due to its higher extractive and protein contents, respectively.

The liquid obtained from the pyrolysis of each residue showed an aqueous phase and an organic phase. The main compounds in the organic phase from SS were carboxylic acids whereas phenols were the main compounds in the organic phase from DM. The aqueous phases from each residue were rich in carboxylic acids, but the aqueous phase from SS also contained amides in large proportions, which explains its higher pH.

The product yields of the co-pyrolysis of SS and DM did not show noticeable

synergistic effects, with the exception of the yields of organic compounds being slightly higher than the predicted average. No remarkable synergistic effects were observed in the liquid phases properties. However, some interactions were detected in the chemical composition of the liquid phases. The proportion of fatty acids decreased and the proportion of aliphatic nitriles increased in the organic phase from the pyrolysis of the SS/DM blend in comparison to the predicted proportions. Finally, no important interactions were found from an energetic point of view. The similar ash contents in SS and DM could explain the small synergistic effect on their co-pyrolysis. Therefore, co-pyrolysis of SS and DM could be a feasible management alternative for these residues in locations where both wastes are generated locally, since the benefits and the drawbacks of the co-pyrolysis are similar to those of the pyrolysis of pure residues.

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