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CATALYTIC AND NON-CATALYTIC PYROLYSIS OF BIOLOGICALLY TREATED MANURE

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Abstract

The utilization of manure for waste-to-bioenergy conversion processes may be a sustainable development choice rather than its traditional use as a fertilizer. Furthermore, the valorization of manure via thermochemical conversion routes and their integration with biological processes can provide an additional pathway in the utilization of residual biomass. On the other hand, the use of metal oxides might enhance the performance of thermochemical processes such as pyrolysis by either cracking the heavy hydrocarbon chains which turns into the production of a higher quality fuel or increasing the H₂ production by promoting secondary reactions as steam reforming or water-gas shift.

The derivative thermogravimetric (DTG) profiles of manure samples could be divided into four general stages: dehydration, devolatilization, char transformation and inorganic matter decomposition. For samples Pre and Dig R, the maximum DTG peaks were obtained at the same temperature. The first peak was lower for sample Dig R due to the removal of organic matter during the anaerobic digestion. On the other hand, the fourth step was not observed for sample Swine, which could be attributed to its low inorganic components (ash) content. The catalysts used in the catalytic pyrolysis process were: CaO, MgO and ZnO. The addition of these oxides modified the corresponding DTG profiles especially for sample Pre. These effects could be also observed in the mass spectra (MS) profile of the samples leading to a higher production of H₂, especially at high temperatures which could be attributed to the enhancement of secondary reactions that usually take place at temperatures higher than 500 °C.

Key words: derivative thermogravimetry (DTG), manure, pyrolysis, thermochemical processes, waste-to-bioenergy

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1. Introduction

Depletion of fossil fuels reserves and the environmental issues derived from their use are the main cause in the increasing attention of the bioenergy production. Currently, the consumption rate is about 91 million barrels per day of oil and 9 billion cubic metres per day of natural gas (BP, 2013). Therefore, the reserves will satisfy 48 years of

oil and 64 years of natural gas supply. In this context, biomass is considered to be one of the few viable replacement options (Shen et al., 2013), contributing approximately 14% to the world annual energy consumption (Shen et al., 2009).

The organic waste such as manure produced in confined animal feeding operations (CAFO) is potentially valuable as fertilizers (Flotats et al., 2009). Thus, the utilization of manure for waste-to-

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bioenergy conversion processes could be a sustainable development choice rather than its traditional use as a fertilizer (Hoppe and Sanders, 2014; Otero et al., 2011). On account of this, a number of bio-processes such as anaerobic digestion (AD) and bio-drying have been proposed in order to value and stabilize these types of wastes. AD has had an increasing attention due to its use for manure stabilization, sludge reduction, odour control and fuel production. AD involves the breakdown of complex organic wastes, producing biogas (mainly composed by methane and carbon dioxide) by a community of anaerobic microorganisms (Callegari et al., 2013; Cantrell et al., 2008). On the other hand, the aim of the bio-drying is the water evaporation by passing air through a waste bed; the heat released by exothermic bio-reactions is captured by an air stream and transferred to water which evaporates (Dufour, 2006). The recovery of the energy released during AD and bio-drying processes is used to obtain high added-value and stabilized products from manure. In this sense, thermochemical conversion such as pyrolysis of biomass is considered to be one of the most direct and promising routes for biomass utilization. Pyrolysis is defined as the thermal decomposition of biomass under an inert atmosphere to obtain three different products: liquid biofuels, gaseous fuel and bio-char.

Thermochemical conversion processes have been widely studied by thermogravimetric analysis (TGA). The valorization of manure as a solid combustible fuel has been recently experienced an increasing attention. Sanchez et al. (2009), compared the combustion of sewage sludge, animal manure and the organic fraction of municipal solid waste by thermogravimetric analysis. Otero et al. (2011) studied the thermal behavior and emissions evolved during swine manure combustion by TGA-MS. It was obtained that the combustion of swine manure started at 390 K and finished at 780 K in two different steps. Moreover, the kinetic behaviour and the activation energy were studied by two different methods: Vyazovkin and Owaza-Flynn-Wall. Wu et al. (2012) examined the pyrolysis and combustion behavior of dairy manure. However, the valorization of manure via thermochemical conversion routes and their integration with biological processes can provide an additional pathway for the utilization of residual biomass that has not been further reported in literature.

In this work, the pyrolysis of two different biologically pretreated manures, dairy (Pre and Dig R) and swine manure (SW), was studied by means of TGA-MS. Finally, the catalytic conversion in the pyrolysis process of manure was compared with that of the non-catalytic one.

2. Material and methods

2.1. Biomasses

In this investigation, the samples used were

animal solid wastes from the province of Québec (Canada). Swine (SW) and dairy manure were the samples selected. They were treated by bio-drying and anaerobic digestion, respectively. Dairy manure was fed into a digester where the anaerobic digestion took place. To evaluate the chemical changes during the biological process, two dairy samples were studied before (sample Pre) and after (sample Dig R) anaerobic digestion.

2.2. TGA-MS analysis

The pyrolysis of manure samples were carried out in a TGA apparatus (TGA-DSC 1, METTLER TOLEDO). The first step is the preheating of the sample at 125 °C; this temperature was kept constant during ten minutes in order to eliminate the moisture content. Subsequently, dynamic runs were carried out up to 1000 °C at a heating rate of 10°C/min under an atmosphere of Ar. TG curves were repeated twice in order to assure reproducibility of results. In previous studies (Sanchez-Silva et al., 2012), the most suitable operating conditions were selected. In this sense, sample weight was kept at 5 mg with a particle size range of 150-200 µm. The flow rate used was 200 Nml/min for pyrolysis tests. The analysis of the gas produced during pyrolysis process was carried out in a mass spectrometer (Thermostar-GSD 320/quadrupole mass analyser; PFEIFFER VACUUM).

2.3. Characterization techniques of manure samples

The manure samples were characterized by Fourier transform infrared spectroscopy (FTIR), bomb calorimeter, elemental analyser and thermogravimetric analyser (TGA).

The IR spectra were recorded on a Perkin-Elmer FTIR Spectrum GX spectrophotometer by accumulating 100 scans (4000 to 800 cm⁻¹) at a resolution of 4 cm⁻¹. 1.5 mg of sample and 150 mg of KBr (spectrometry grade) were homogenized thoroughly in an agate mortar, pelletized and then analysed. The heat of combustion was determined using a Parr 1356 bomb calorimeter according to UNE 164001:2005 EX at constant volume and a reference temperature of 25 °C. The energy equivalent of the calorimeter was determined with a standard reference sample of benzoic acid. A known mass amount of the samples were introduced in a gelatine capsule and combusted under an oxygen atmosphere. The ultimate analysis was used to measure the carbon (C), hydrogen (H), nitrogen (N), oxygen (O) and sulfur (S) content of a sample. This analysis was performed following the standard UNE-EN 15104:2011. The equipment used in this analysis is capable of detecting all elements cited by various mechanisms and the result is obtained as a mass percentage of each element in dry basis.

The proximate analysis was used to determine the ash and the volatile matter content of the samples. The equipment used to perform the proximate

analysis was a thermogravimetric analyzer (TGA / DSC Model 1 METTLER TOLEDO STAR[®]System).

2.4. Catalyst

Calcium oxide, magnesium oxide and zinc oxide were selected as catalysts. Firstly, the oxides were calcined at 1000 °C for 2 h to eliminate the water present both as humidity and bonded with the crystals. Furthermore, the calcination was carried out before experiments to ensure the stability of the oxides at the working temperature range.

3. Results and discussion

3.1. Characterization of dairy and swine manure

The ultimate analysis, the weight percentage of volatile matter (VM) and ash and the calorific values (HHV) of manure samples are shown in Fig. 1. As it can be seen, carbon and hydrogen content were higher for sample Pre whereas sample SW contained a higher content of nitrogen, sulphur and oxygen. The VM content was lower for sample Dig R than for the Pre one which was attributed to the biological degradation of the manure organic matter during the anaerobic digestion (AD) of sample Pre (Tambone et al., 2009). Furthermore, a higher amount of ash was observed for sample Dig R due to its lower volatile matter content (Kobayashi et al., 2013; Thygesen and Johnsen, 2012).

The HHV of sample Pre (18.4 MJ/kg) was higher than that for the SW one (16.1 MJ/kg) which could be associated to the high carbon and hydrogen content of sample Pre. Furthermore, sample SW showed a higher nitrogen and oxygen content which decreased the calorific energy of the sample (Channiwala and Parikh, 2002). On the other hand, the calorific value of sample Dig R was lower than that of sample Pre in spite of the similar values of their ultimate analysis (C, H and N contents). This fact can be explained by the high ash content of sample Dig R which diminished the available energy of the fuel (McKendry, 2002). Nevertheless, calorific values for the samples under study are within a similar range to other types of biomass (12-20 MJ/kg) (Choi et al., 2014) pointing out their suitability for their energetic valorisation.

3.2. Thermogravimetric study on pyrolysis of manure samples

The thermogravimetric (TGA) and derivative thermogravimetric (DTG) profiles of the pyrolysis process of samples Pre and Dig R at a heating rate of 10 °C/min are shown in Fig. 2.

The pyrolysis process of dairy samples (Pre and Dig R) could be divided into five stages. The first one appearing at temperatures below 125 °C represented the drying process of samples (dehydration stage).

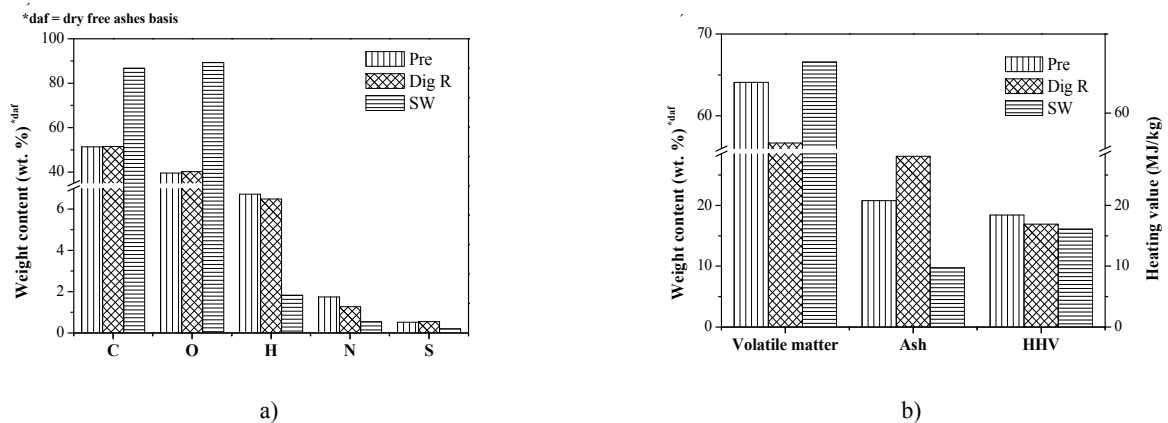


Fig. 1. Manure samples characterization: a) Ultimate analysis and b) Volatile matter, ash and calorific value

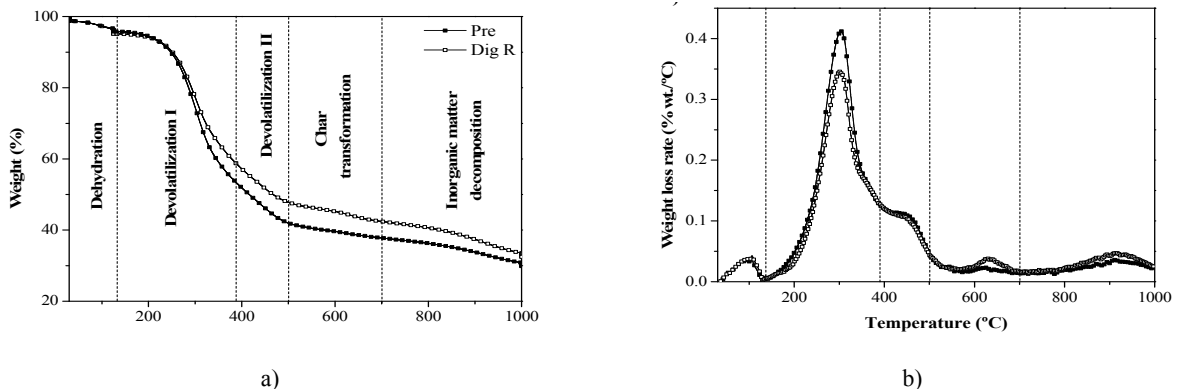


Fig. 2. Thermogravimetric profiles for the pyrolysis process of samples Pre and Dig R: a) thermogravimetric (TGA) profile and b) derivative thermogravimetric (DTG) profile

The second step occurred between 200 and 390 °C where the volatile matter was decomposed. In this stage, the maximum decomposition rate took place at 300 °C, being associated with hemicellulose and glucoside linkage depolymerisation (Wnetrzak et al., 2013). The maximum weight loss in samples Pre and Dig R (approximately 50 wt.% and 40 wt.%, respectively) took place in this stage, being considered the main pyrolytic stage. The lower weight loss and decomposition rate found for sample Dig R pointed out, as above mentioned, the removal of organic matter during the anaerobic digestion.

The third stage was characterized by a shoulder appearing between 390 and 500 °C in the DTG curves. This shoulder was ascribed to the decomposition of lipids and other N-containing compounds (Wnetrzak et al., 2013). Both the second and the third stages were considered as the devolatilization stages.

The last two stages were identified by two peaks between 550-700 °C and 800-1000 °C, associated with the decomposition of the formed char and the decomposition of inorganic matter (López-González et al., 2013).

Sample Dig R presented, in these last stages, peaks more prominent, which was related, as expected, to its higher ash content (Fig. 1). Fig. 3 shows the TGA-DTG profiles for the pyrolysis of sample SW at a heating rate of 10 °C/min.

As it can be seen, the DTG profile for the pyrolysis process of sample SW showed four stages (Fig. 3). The last fifth step was not observed in this sample, which could be attributed to the lower amount of ashes generated (Fig. 1). The main degradation stage was developed in a similar temperature range as that observed for dairy samples. However, this stage was characterized by the presence of two peaks at 280 °C and 320 °C, which could be associated to the thermal decomposition of hemicellulose (Sanchez-Silva et al., 2012).

This result is consistent to the fact that swine are not ruminant and therefore hemicellulose is low degraded in its intestines.

Regarding sample SW, the shoulder of the third stage is smaller than that observed in samples Pre and Dig R. Furthermore, there was a small peak close to 700 °C that could be attributed to the decomposition of some mineral components (Wnetrzak et al., 2013).

3.3. Analysis of gases evolved during pyrolysis of manure samples

Mass spectrometry (MS) profiles for the pyrolysis of samples Pre, Dig R and SW are shown in Fig. 4. MS spectra of manure samples could be divided into different stages associated to their degradations steps studied in the TGA/DTG profiles and described in the previous section. Generally, in the first step (dehydration) water was mainly detected for all the samples.

In the first devolatilization stage, most gaseous products were found, obtaining the highest yields for CO and CO₂ with a higher proportion of the last one. CH₃SH were the only sulphur product detected in this stage. In turn, nitrogen compounds such as amines and cyanides were also identified. In the second devolatilization stage, nitrogen compounds and CH₄ were the main emission peaks found besides aromatic compounds such as toluene. H₂ started evolving in this stage, indicating that char transformation reactions such as thermal cracking and dehydrogenation were taking place (Sanchez-Silva et al., 2012). Additionally, CO, CO₂, HCN and CH₄N were also detected in all samples at 1000 °C (inorganic matter decomposition stage). However, HCN was not detected in sample Pre. Finally, the main gaseous products found in all the stages for dairy samples were similar to those found for SW sample.

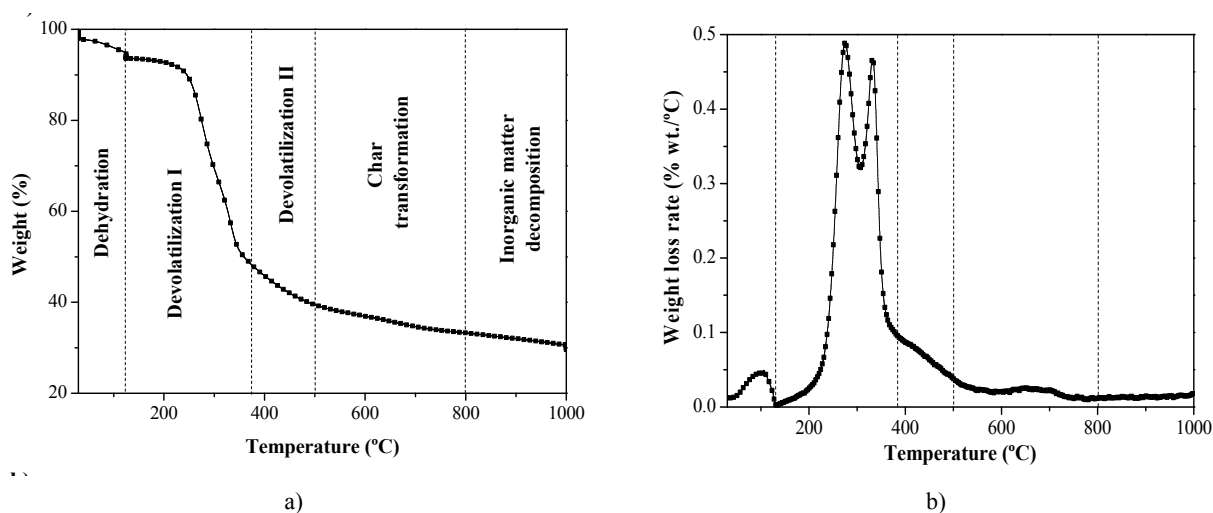


Fig. 3. Thermogravimetric profiles for the pyrolysis process of sample SW: a) thermogravimetric (TGA) profile and b) derivative thermogravimetric (DTG) profile

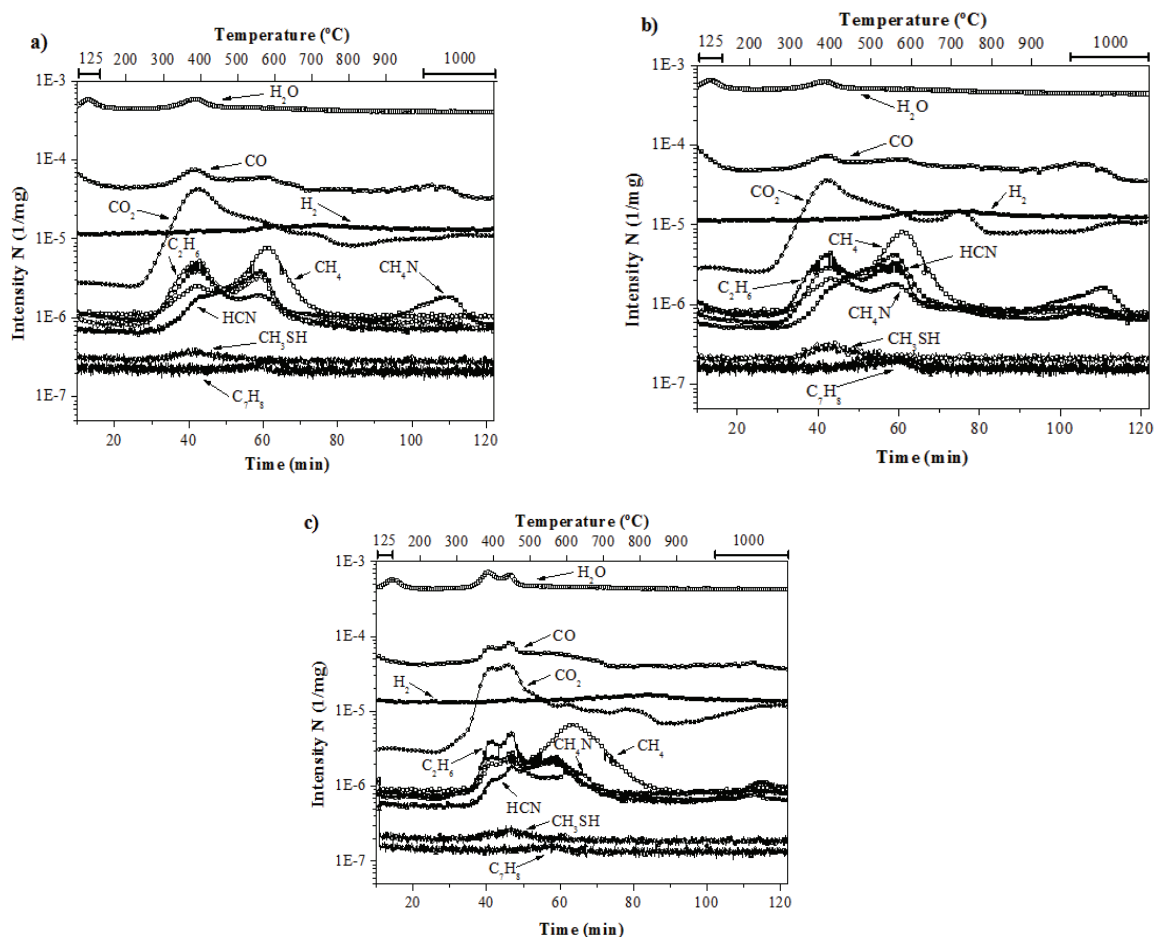


Fig. 4. Mass spectra for the pyrolysis process of manure samples: a) Pre, b) Dig R and c) SW at 10°C/min

3.4. Manure pyrolysis using catalysts

Sample Pre was the sample selected for the study of the pyrolysis using oxides as catalysts.

The derivative thermogravimetric (DTG) curves of the pyrolysis process at a heating rate of 10 °C/min of the sample Pre with and without catalyst are shown in Fig. 5. Mass spectrometry profiles for the pyrolysis of Pre sample by using different catalysts are shown in Fig. 6 (CaO), Fig. 7, (MgO) and Fig. 8 (ZnO). It can be observed that oxides had not effect on the maximum weight loss temperature at the second stage of the pyrolysis process. However, the addition of these oxides decreased the maximum weight loss in all cases, following the decreasing order: Pre>Pre+MgO>Pre+ZnO>Pre+CaO.

In the third stage of the pyrolysis process, this effect was negligible except for the addition of ZnO which reduced the weight loss by a factor of two.

There was a significant weight loss in the fourth stage (between 600 and 700 °C) for the sample with CaO whereas the rest of the samples showed the same behavior. This fact can be attributed to the decomposition of the CaCO₃ formed in previous stage where the CO₂ evolved can be adsorbed by the CaO (Han et al., 2010). The temperature range of the fourth stage is the typical for the degradation of

carbonates (Han et al., 2010). Besides, the MS profile of CO₂ showed a peak between 600 and 700 °C (Fig. 6), pointing out the release of this compound during the carbonate decomposition. In the last stage there was no difference in the DTG profiles of the samples except for ZnO one. This profile showed a prominent peak between 800 and 1000 °C (Fig. 5). The evolved gases at this temperature range were CO₂, CO, H₂, C₂H₅⁺ and C₂H₂. It can also be observed a decrease of the intensity of the water profile (Fig. 8).

Water can react either with the oxygenated hydrocarbons formed during the pyrolysis process or with the char remained, leading to CO and H₂ formation by steam reforming (Eq. 1) in the presence of ZnO (Maciel et al., 2011).

On the other hand, water gas shift reaction could also take place in the present of this catalyst (Maciel et al., 2011). These two reactions could explain the presence of CO₂, CO and H₂ at the last stage of the pyrolysis process (Fig. 8).

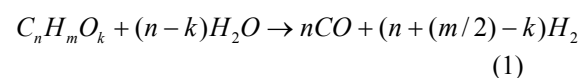


Fig. 9 shows a zoom of the H₂ profiles for sample Pre without and with catalysts. It can be observed that the ZnO was the oxide which best promoted the formation of H₂.

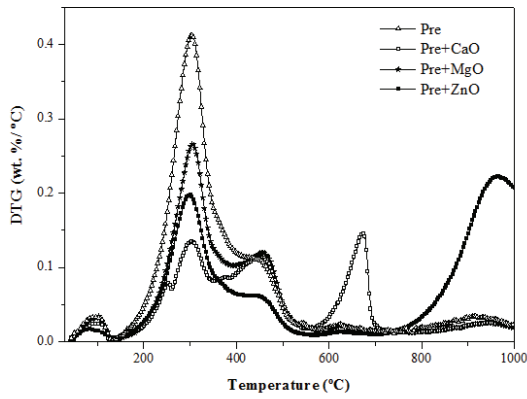


Fig. 5. Derivative thermogravimetric curves for the pyrolysis process of sample Pre without and with catalysts: CaO, MgO and ZnO

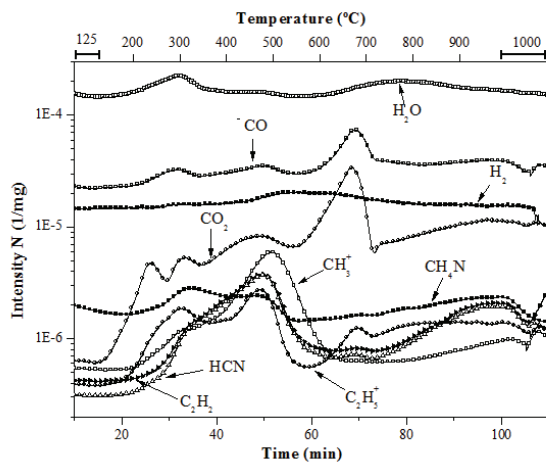


Fig. 6. Mass spectra of the pyrolysis process at 10°C/min of sample Pre with CaO

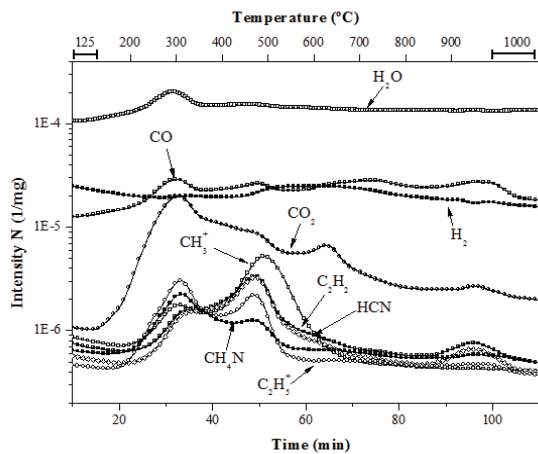


Fig. 7. Mass spectra of the pyrolysis process at 10°C/min of sample Pre with MgO

4. Conclusions

The pyrolysis process of manure samples could be divided into five stages: dehydration, two devolatilization stages, char transformation and inorganic matter decomposition. The fifth step was

not observed for sample SW which could be attributed to its lower amount of ashes. The lowest weight loss and decomposition rate were found for sample Dig R, pointing out the removal of organic matter during anaerobic digestion.

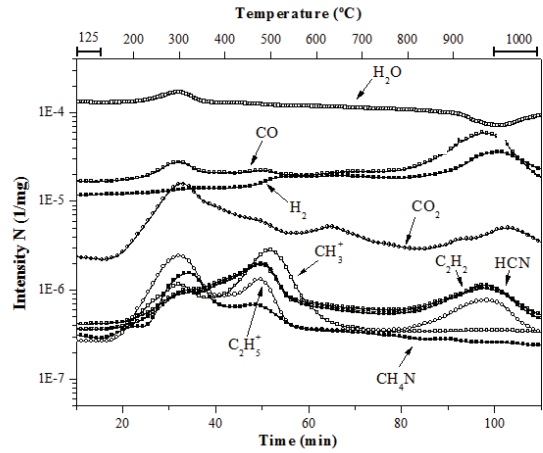


Fig. 8. Mass spectra of the pyrolysis process at 10°C/min of sample Pre with ZnO

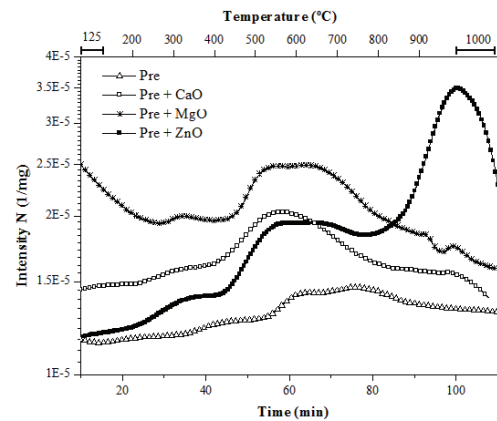


Fig. 9. Zoom of the H₂ production with and without catalysts

The addition of oxides as catalyst during the pyrolysis process of sample Pre decreases the temperature range in which the maximum weight loss was taken place. The maximum weight loss also decreased due to the oxides can adsorb the CO₂ present, leading to carbonates.

The more prominent effect was the H₂ formation at the end of the pyrolysis process with ZnO. The gasification with steam of the char formed at this temperature can take place and could be promoted by the presence of this oxide.

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