



Life cycle assessment of swine and dairy manure: Pyrolysis and combustion processes



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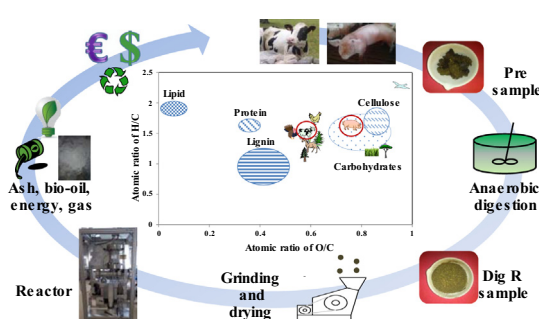
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HIGHLIGHTS

- Pyrolysis and combustion processes of three manure samples were studied by TGA–MS.
- The economic viability, energetic and environmental impacts were evaluated by LCA.
- The main components of the gas produced were: H₂, CH₄, CO, C₂ hydrocarbons and CO₂.

GRAPHICAL ABSTRACT



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ABSTRACT

The valorization of three different manure samples via pyrolysis and combustion processes was evaluated. Dairy manure (sample Pre) was biologically pretreated by anaerobic digestion (sample Dig R) whereas swine manure (sample SW) was pretreated by a biodrying process. Thermal behavior of manure samples were studied by means of thermogravimetric analysis coupled with mass spectrometry (TGA–MS). These processes could be divided into four general stages: dehydration, devolatilization, char transformation (oxidation for combustion) and inorganic matter decomposition. The main differences observed among the samples were attributed to their different composition and pretreatment. The economic feasibility, energetic and environmental impacts of pyrolysis and combustion technologies for dairy samples were carried out by means of life cycle assessment (LCA) methodology. Four different scenarios were analyzed. The economic feasibility of the pyrolysis process was demonstrated, being sample Dig R the best environmental option. However, the combustion of sample Pre was the best energetic option.

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1. Introduction

The production of bioenergy is attracting increased attention due to the depletion of fossil fuel reserves and the environmental

issues derived from their use. At the current consumption rate (84 million barrels per day of oil and 284.5 billion cubic feet per day of natural gas (BP, 2010)), the reserves will satisfy 48 years of oil and 64 years of natural gas supply. In this scenario, biomass is considered to be one of the few viable replacement options (Shen et al., 2013), contributing to approximately 14% to the world's annual energy consumption (Shen et al., 2009).

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Organic waste from livestock, such as manure, is potentially valuable as fertilizers (Flotats et al., 2009). However, the manure produced in confined animal feeding operations (CAFO) is highly concentrated in some regions, exceeding the needs of farmland. In this regard, the produced manure surplus proposes economic and environmental liabilities (Sweeten et al., 2003). Thus, the utilization of manure and other organic-based wastes as bioenergy feedstock for waste-to-bioenergy conversion processes may be a sustainable development choice rather than its traditional use as a fertilizer (Otero et al., 2011). On this account, several bio-processes such as anaerobic digestion (AD) and bio-drying have been proposed in order to value and stabilize these types of residues.

AD has had a revival of interest due to the fact that it is used for manure stabilization, sludge reduction, odour control and fuel production. AD involves the breakdown of complex organic wastes, producing biogas (mainly methane and carbon dioxide) by a community of anaerobic microorganisms (Cantrell et al., 2008). On the other hand, the bio-drying process partially removes the waste moisture 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. The aim of bio-drying is so that the water evaporation has the lowest conversion of organic carbon to carbon dioxide (Dufour, 2006).

The recovery of the energy released during bio-reactions of AD and bio-drying is used to obtain high added-value and stabilized products from manures. In this sense, thermochemical conversion of biomass is considered as one of the most promising and direct routes for biomass utilization. Combustion is based on the complete oxidation of biomass organic wastes to produce energy in the heat form. Pyrolysis is the thermal decomposition of biomass under an inert atmosphere that produces liquid biofuels, a gaseous fuel and bio-char.

Thermogravimetric analysis (TGA) has been widely used for the study of thermochemical conversion processes. Kok & Özgür studied the effect of co-firing of biomass fuels with oil shale (Özgür et al., 2012) and the combustion behavior of agricultural residues and its kinetics (Kok and Özgür, 2013). On the other hand, the interest to valorize manure as a solid combustible fuel has recently experienced an increased interest. Apart from the technology, it is important to study the impact of these thermochemical processes from an energetic, environmental and economic point of view. Life cycle assessment (LCA) is an appropriated tool for estimating the energy consumed or generated and the potential environmental impacts of the thermochemical process considered (Roberts et al., 2009).

In this work, the pyrolysis and combustion processes and the evolved gasses of two different manures (dairy and swine manure) by means of TGA coupled with mass spectrometry (MS) were studied. Furthermore, the effect of AD and bio-drying pretreatments on the thermal behavior of manures was evaluated. Finally, a LCA was used to estimate and compare the energy requirements, the greenhouse gas (GHG) emissions and the economic feasibility of the pyrolysis and combustion of dairy samples before and after biological pretreatment. The main aim is to compare both the pyrolysis and the combustion processes from the energetic, environmental and economic point of view using experimental data obtained from thermal analysis coupled with MS. This kind of studies is important to decide what process and what biomass is more suitable from the industrial point of view.

2. Methods

2.1. Biomasses

The samples used in this investigation were solid animal wastes obtained 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. Firstly, dairy manure was stored in a tank. Subsequently, the sample was fed into the digester where the anaerobic digestion took place. To assess the chemical changes during the biological process, two dairy samples were studied: one coming from the storage tank output (Pre) and another one coming from the digester output (Dig R).

Fig. 1 shows the classification of manure samples based on a Van Krevelen diagram (plot of H/C versus O/C atomic ratios on a dry ash free basis (daf) of the biomass). This type of diagram is used to classify different types of fuel according to their H/C and O/C atomic ratios. The groupings of individual biomolecular compounds were adapted from Kim et al. (2003) to include not only lipids, protein and carbohydrates but also lignin and cellulose (Hammes et al., 2008). Some lignocellulosic biomass (Pine, Fir and Eucalyptus) and the microalgae *Chlorella vulgaris* used in previous studies (López-González et al., 2014a, 2013) were represented along with different animal manures (chicken, turkey, horse and seabird) (Li et al., 2013; Lundgren and Pettersson, 2009). In addition, dairy and swine manure were plotted on the Van Krevelen diagram in order to compare them to the other biomasses. It was observed that positions in the diagram were very different. Due to their differences, dairy and swine manure were selected to be investigated.

The sample preparation was done following the same steps as the reported by López-González et al. (2014b). The samples were dried in an oven for 5 h, milled and sieved to an average particle size between 150 and 200 μ m.

2.2. TGA–MS analysis

The pyrolysis and combustion of manure samples were carried out in a TGA apparatus (TGA-DSC 1, METTLER TOLEDO). The first step in pyrolysis and combustion experiments consisted of sample preheating at 125°C; this temperature being maintained for 10 min in order to remove the moisture content. Subsequently, dynamic runs were carried out, in the case of pyrolysis experiments, up to 1000 °C at a heating rate of 10 °C/min under an atmosphere of Ar and, in the case of combustion runs, to 900 °C under a reactive atmosphere of 21 vol.% of oxygen and 79 vol.% of Ar. TG curves were repeated twice in order to ensure the reproducibility of results. The experimental error of these measurements was calculated, obtaining an error of $\pm 0.5\%$ in the weight loss measurement and $\pm 2^\circ\text{C}$ in the temperature measurement.

In previous studies (Sanchez-Silva et al., 2013), the most suitable operating conditions were selected. In this instance, sample

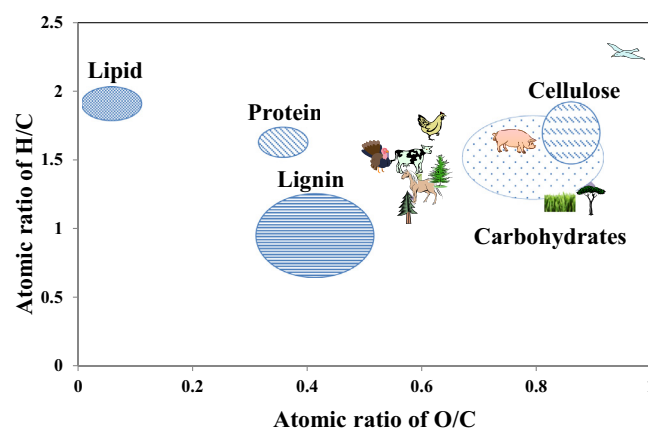


Fig. 1. Regional plots of elemental compositions from some main biomolecular components, lignocellulosic biomass, *Chlorella vulgaris* microalgae and the dairy and swine manure studied on the Van Krevelen diagram.

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