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Thermochemical conversion of animal by-products and rendering products

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ABSTRACT

This paper presents a preliminary study of the characterization of real waste from slaughterhouses as well as their rendering products (protein and fat) through different pyrolytic techniques: thermogravimetric analysis (TG), analytical pyrolysis in a pyroprobe equipment and hydrothermal liquefaction process (HTL). The experiments have allowed a deeper knowledge about the thermal behavior of these wastes under different conditions: slow pyrolysis up to 800 °C (TG), flash pyrolysis at 500 °C and room pressure (pyroprobe) and slow pyrolysis at 290 °C and 110–130 bar (HTL batch reactor). Experiments with each one of the materials (real waste, PAP and fat) as well as some mixtures have been performed. Gas chromatography and mass spectrometry techniques were used to identify the pyrolytic products obtained. The results indicate that fatty acids and fatty esters are the major group obtained in the pyrolysis of fat samples, followed by aliphatic hydrocarbons. In the case of PAP pyrolysis, heterocyclic aromatic compounds, which includes typical products coming from protein degradation, is the major group obtained. Oxygenated aliphatics are also obtained in high amounts. In the case of the HTL experiments, significant glycerine amounts were detected in the aqueous phase. The yield of biocrude obtained under HTL conditions is about 30%, with a high proportion of nitrogenated compounds (amides, pyrrole and pyridine derivatives). Generation of amides is much higher under HTL conditions than in the analytical pyrolysis runs while the proportion of acids is reduced.

1. Introduction

Animal by-products (ABP) are wastes from different origins (slaughterhouses, butcher's shops, restaurants or houses). Over 20 million tons are being generated annually in the European Union (EU) (European Commission website) that can be dangerous if they are not properly disposed of. Nowadays, animal by-products are mainly treated by a rendering process in order to meet the European regulation. During the rendering, the waste is kept at 133 °C and 3 bar for 20 min. This process removes water from the material and separates fat from the bone and protein fraction. In the EU, the meat and bone fraction is called meat and bone meal (MBM) if the ABPs are classified in categories 1 and 2 (high risk); when ABPs are classified in category 3 (low risk and suitable for human consumption) the same fraction is named processed animal protein (PAP).

In general, MBM represents a significant amount of waste that has to be disposed of. Disposal in landfills (Cascarosa et al., 2012) and co-combustion in cement kilns are two current treatments for this type of wastes. However, due to the emissions as well as social concern about environmental problems generated by the incineration of MBM, this alternative has many detractors and other environmentally friendly options need to be found (Cascarosa et al., 2011).

The pyrolysis or gasification of MBM could be a suitable alternative to the combustion process. The thermal behavior of MBM has been studied using different systems, such as fixed bed reactor (Ayllón et al., 2006), bubbling fluidized bed reactor (Berruti et al., 2012) or fluidized bed gasifier (Campbell et al., 2012). A previous characterization of the material that is going to be pyrolysed, gasified (or burnt) provides useful information to design the reaction

Abbreviations: ABP, animal by-products; HTL, hydrothermal liquefaction; PAP, processed animal protein; MBM, meat and bone meal; LHV, low heating value; TGA, thermogravimetric analysis; GC, gas chromatography; FID, flame ionization detector; GC-MS, gas chromatography–mass spectrometry; Py/GC-MS, pyroprobe connected online with a gas chromatography-mass spectrometry.

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system as well as the product treatment processes. Thus, a significant number of references about physical and chemical characterization of MBM are found in the review of MBM thermochemical processing developed by Cascarosa et al. (2012). In general, the sample analyses indicate high ash percentage, attributed to the presence of bones in the feedstock and high oxygen and nitrogen content.

Thermogravimetric analysis (TGA) is also a widely used technique to study solid decomposition processes under different reaction environments. The thermal behavior of many different biomasses, including MBM, has been studied using this technique (Chaala and Roy, 2003; Conesa et al., 2003; Senneca, 2008). A thermogravimetric analysis shows the different processes overlapped in the thermal decomposition of this type of materials.

Analytical pyrolysis has also been extensively used to obtain information about the composition of different organic materials. Many types of biomass have been pyrolyzed in equipments connected online to analytical systems with the aim of studying either composition of the original sample or the decomposition products generated: for example, cellulose (Funazukuri et al., 1987), wood (Maniatis and Buekens, 1989), urban solid waste (García et al., 1992), klason lignin (Caballero et al., 1993) ancient papyrus (Martínez et al., 2001), paint binders (Learner, 2001), organic pigments (Brosseau et al., 2009) or microalgae samples (Valdés et al., 2013). No information about analytical pyrolysis of animal by-products has been found, although some references related to general pyrolysis of this type of wastes have been published (Ben Hassen-Trabelsi et al., 2014; Bujak and Sitarz, 2016).

Another thermochemical process used with different biomass is the hydrothermal liquefaction (HTL). This involves the use of water and pressure together with temperature in a pyrolysis process. HTL operates at subcritical water conditions, around 250–370 °C and 10–22 MPa. This process can play a key role in the biofuel production from wet biomass, since the step of feedstock drying, typical in a conventional pyrolysis, can be avoided. This fact would reduce the operational costs significantly (University of Alicante, 2017. Deliverable 3.7.). Furthermore, the process shows other benefits by using water as an extraction solvent. Some review papers about this technique have been published (Toor et al., 2011; Pavlovič et al., 2013; Xue et al., 2016). Most of the studies found investigate the characteristics of algal biomass as a feedstock for hydrothermal liquefaction, due to its high moisture percentage (Biller et al., 2012; Vardon et al., 2011; Brown et al., 2010; Dote et al., 1994); other papers refer to the liquefaction of wood (Zhong and Wei, 2004; Haarlemmer et al., 2016). Few references related to animal by-products (cattle manure, swine carcasses, waste meat) have been found (Xiu et al., 2010; Yin et al., 2010; Zheng and Kong, 2014; Zheng et al., 2015).

Valuable compounds could be recovered by pyrolysis of ABPs. However, such products were obtained in the form of mixture. Depending on the end product utilization, additional separation and purification would be needed, thus involving additional cost for treatment.

The aim of this work is focused on the characterization of a category 3 typical waste from slaughterhouses as well as of their rendering products (PAP and fat), to evaluate their use as source of fuels or added value products. Although PAP and fat have practical applications, there is an increasing interest in alternative no risk treatments for MBM. In this sense, the study of the thermal behavior of PAP and fat mixtures can provide valuable information about the characteristics of the bio-oil that could be obtained from them, thus contributing to solve the problem of disposal of this type of wastes. Three techniques have been used in the study: thermogravimetric analysis, flash pyrolysis in a pyroprobe equipment and HTL process in a batch reactor.

2. Materials and methods

2.1. Materials

The experiments were carried out with two types of materials: the real raw waste from porcine and bovine origin in a proportion 60/40 respectively and the final products (PAP and fat) of rendering of this real waste, both supplied by an animal by-products rendering company.

A manual classification of the components of the raw material allowed a rough estimation of its composition: around 22% bones, 39% skin and 39% fat, meat and blood, mainly.

Table 1 shows the characteristics of the samples used without any previous treatment. In order to characterise the PAP, fat and the real waste used, the moisture and ash content as well as the ultimate analysis and the low heating value determination were carried out. The ultimate analysis determines the amount of carbon, hydrogen, nitrogen, oxygen, sulfur and other elements within the sample.

The ash content was obtained gravimetrically by combustion of the samples at 815 °C for 1 h in a muffle furnace (EN ISO 1171:2010). The moisture content was measured by oven drying to constant weight at 105 °C (EN ISO 18134-1:2015). The proportions of carbon, hydrogen and nitrogen in the different samples were determined using an Elemental CHNS Microanalyzer, with Micro TruSpec detection system from LECO. Elemental chemical analysis of the elements between F and U was performed with sequential X-ray spectrometer Philips Magic Pro PW2400. For the low heating value determination, the combustion of samples was performed in a Leco Corporation calorimetric bomb AC-350 model.

In order to simulate the real waste (containing around 50% moisture), a mixture of PAP and fat from a rendering process of a raw material of 60/40 porcine/bovine origin, and water was prepared. The corresponding percentages were estimated from the fat and PAP content of porcine and bovine animal by-products samples shown in Table 2 (ACINCA FENAVE database, Tacon, 1989) in water free basis, the percentage according to the different sample origin used in the rendering process (i.e.: 60/40) and the water content of our real waste (50%). Consequently, the water content of our real sample is 50% and that for fat and PAP are calculated according to Eqs. (1) and (2):

$$\%F = 50\left(\frac{0.6F_P}{F_P + PAP_P} + \frac{0.4F_B}{F_B + PAP_B}\right) \quad (1)$$

$$\%PAP = 50\left(\frac{0.6PAP_P}{F_P + PAP_P} + \frac{0.4PAP_B}{F_B + PAP_B}\right) \quad (2)$$

where F_P and PAP_P are the fat and PAP content in the porcine sample in wet basis, and F_B and PAP_B are the fat and PAP content in the bovine sample in wet basis.

2.2. Thermogravimetric analysis (TGA)

TGA analyses were performed using a Thermobalance METTLER TOLEDO, model TGA/SDTA851e/SF/1100. Approximately 6 mg of each sample were heated from 25 to 800 °C in a nitrogen atmosphere (50 ml/min) with a heating rate of 10 °C/min. The temperature of the sample was measured with an R type thermocouple located under the crucible.

The equipment was calibrated using indium and aluminium standards and periodic checks have been made to ensure that the equipment remained in good conditions according to the calibration specifications.

Four replicates of each sample were performed. Real waste shows the highest dispersion of the results due to its heterogene-