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Physical and chemical characterisation of crude meat and bone meal combustion residue: "waste or raw material?"

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Abstract

As a result of the recent bovine spongiform encephalopathy (BSE) crisis in the European beef industry, the use of animal by-product is now severely controlled. Meat and bone meal (MBM) production can no longer be used to feed cattle and must be safely disposed of or transformed. Main disposal option is incineration, producing huge amounts of ashes the valorisation of which becomes a major concern. The aim of this work is to characterise MBM combustion residue in order to evaluate their physical and chemical properties to propose new valorisation avenues. The thermal behaviour of crude meat and bone meal was followed by thermogravimetric analysis (TGA) and (24 wt.%) inorganic residue was collected. The resulting ashes were characterised by powder X-ray diffraction (XRD), particle size distribution, specific surface area (BET), scanning electron microscopy (SEM) couple with energy disperse X-ray analysis (EDX). Elemental analysis revealed the presence of chloride, sodium, potassium, magnesium with high level of phosphate (56 wt.%) and calcium (31 wt.%), two major constituents of bone, mainly as a mixture of $Ca_{10}(PO_4)_6(OH)_2$ and $Ca_3(PO_4)_2$ phases. The impact of combustion temperature (from 550 to 1000 °C) on the constitution of ashes was followed by TGA, XRD and specific surface measurements. We observed a strong decrease of surface area for the ashes with crystallisation of calcium phosphates phases without major changes of chemical composition.

Keywords: Meat and bone meal; Apatite; Ashes; Phosphate sources; Valorisation

1. Introduction

As a result of the recent bovine spongiform encephalopathy (BSE) crisis in the European beef industry, the use of animal by-products is now severely restricted. Indeed, the transmissible spongiform encephalopathy agent (SPE agent), also named scrappy prion, is responsible for fatal neurodegenerative diseases in animals and humans [1–4]. Nowadays, brain, spinal cord, tonsils, etc. and sick animal corpses are considered as high risk wastes and must be incinerated. Safe animal wastes (meat and bones) coming from slaughterhouse waste are mixed, crushed and cooked together. After the cooking process, tallow is extracted and the remaining residue, known as meat and bone meal (MBM) or animal flour, is sterilised before being safely disposed off [5–7]. This sterilised product is called low risk MBM. Since November 2000, low risk MBM can no longer be used to feed cattle but can be incorporated in food for pig, poultry, fish or animal pets. Their import to European Community (EU) and their export from EU is banned. Nowadays, the over production of low risk MBM must be eliminated or safely recycled [5–10].

Among the different processes studied, valorisation of MBM can be realised by a thermal degradation treatment (incineration or pyrolisis) [8–10], as they are readily flammable fuel (approximately 17,000 kJ kg^{-1}) [9]. During high temperature combustion (over 800 °C), thermal energy is recovered and proteins such as prions are destroyed (as all organic matter is converted to CO_2, H_2O, etc.) [1–3]. Co-incineration in cement kilns is the most common way, for MBM destruction, used in France. They are mixed with cement compounds (calcium, silica, alumina, etc.) and heated over 1500 °C to pro-

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duce the clinker. In England, the use of MBM dedicated incinerator is developed. Incineration plants are set up in Glanford, Wyminton and Widnes with a joint capacity of 205,000 tons of MBM/year (ton = Mg).

In France, for example, 850,000 tons of MBM are produced each year but actually only 45% can be burned by cement plants [6]. The remaining 55% are stored waiting for further destruction or valorisation. Ashes produced by meat and bone meal combustion represent up to 30% of the original weight. Thermal treatment of the entire MBM production would lead to an important amount of ashes (nearly 250,000 tons/year). Therefore, the fate of meat and bone meal combustion residue stocks is of major environmental concern. Large storage costs for wastes classified as dangerous are also an economic burden.

As MBM combustion residues mainly arise from bone combustion, they contain a high amount of phosphate and calcium, two major constituents of bone. In our search for new valorisation ways we focus on phosphoric acid production, phosphate source for industry, agricultural soil enrichment, heavy metals immobilisation in soil or water, etc. as developed for other phosphate rich materials (rocks, hydroxyapatites, bone char, etc.) [11–30]. We report here a study on the physical and chemical characterisation of meat and bone meal combustion residues. The thermal behaviour of crude MBM was followed by thermogravimetric analysis (TGA). The impact of combustion temperature on the structure of ashes was followed by powder X-ray diffraction. The resulting ashes were characterised by elemental analysis, powder X-ray diffraction (XRD), particle size distribution, specific surface area (BET), scanning electron microscopy (SEM) and energy disperse X-ray analysis (EDX).

2. Materials and methods

Low risk sterilised meat and bone meal were provided by Fersobio. MBM were burned twice by calcination in an electric furnace programmed to reach 550 °C at 2°/min. During combustion, MBM particles melted and sticked together. The first combustion gave a black residue (carbon rich). This residue was mixed manually before a second combustion in order to complete decomposition and obtain clear ashes.

Thermogravimetric analysis was performed with a Setaram TG-DTA92 analyser, in a platinum crucible, under air or argon atmosphere, from 20 to 1000 °C with an increasing temperature rate of 3 °C/min. The mass of the samples used was 40 mg approximately.

Total C, H and N were determined by elemental analysis on a Thermoquest CHN EA 1108W. Specific surface area measurements were realised by applying a 5-points BET method (nitrogen adsorption at 77 K) on a Micromeritics Gemini Vacprep 061. Samples were previously degassed under vacuum at 100 °C.

Electron scanning microscopy (SEM) observations coupled with EDX analysis were performed on a Philips ESEM XL30 environmental microscope. Infrared spectra were recorded with an ATI Mattson (Genesis series FTIR) spectrometer.

Powdered solids were analysed by X-ray diffractometry using a Siemens D501 diffractometer operating with Co Kα radiation (1.78892 nm; 30 kV; 35 mA). Measurements were made using a step-scanning technique with 2θ step intervals of 0.029° from $0.29° < 2\theta < 105°$ and an acquisition time of 1 s/step. Phases were identified by comparing the pattern with JCPDS files (Joint Committee for powder diffraction standards).

Particle size analysis was performed on a laser (He–Ne at 632.8 nm) diffraction analyser (Mastersizer S, Malvern) equipped with a solution dispersion accessory (Hydro QS-MU, Malvern) in pure ethanol solution. $D(V,0.5)$ and $D(V,0.9)$ values are the maximum particles size for particles representing, respectively 50 and 90% of sample volume.

Elements analysis was performed by atomic adsorption (AA) with flame atomisation (Unicam, solar, air/C_2H_2 gas mixture), with graphite furnace atomisation (Perkin-Elmer SIMA 6000) or inductively coupled plasma (ICP). Certified aqueous standards and matrix modifier [$LaCl_3$, $Mg(NO_3)_2$ and $NH_4(H_2PO_4)$] were obtained from Aldrich.

3. Results and discussion

3.1. MBM combustion

In our experiments we used low fat MBM coming from slaughterhouse waste. These products are dehydrated (110 °C/4–5 h) and sterilised (133 °C/20 min/3 bar) according to European standards by Fersobio. Resulting low risk MBM still contains water (3–8 wt.%) and large amount of fats (10–14 wt.%) and other organic compounds (25–35 wt.%) according to low risk MBM producers [6].

Thermal analysis of MBM is realised under air (combustion) and argon (pyrolysis) atmosphere with 3 °C/min temperature increase rate (Fig. 1). Combustion shows a three step mass loss with nearly 24% inorganic residue available. We can notice that the first two steps are similar in both experiments (air and Ar). The first step, in the temperature range of 50–150 °C, is attributed to water (6%) evaporation. The second step, observed between 180 and 300 °C, is due to evaporation of low molecular weight compounds and/or decompositions reactions. At last, the third weight loss between 250 and 500 °C, faster under air than under argon atmosphere, is a combustion stage, where all organic mater is decomposed to H_2O, CO_2, etc. Under our conditions, thermal decomposition is practically complete at 550 °C. Crude ashes represent 24 wt.% of the initial MBM. Elemental analysis reveals small amounts of carbon (0.97%), hydrogen (0.27%) and nitrogen (0.23%) confirming the inorganic nature of ashes. We notice that over 550 °C mass loss is stabilised, suggesting that the composition of the ashes remains almost unchanged. These results are in agreement with previous studies on