ELSEVIER

Chemosphere 59 (2005) 85–90

CHEMOSPHERE

www.elsevier.com/locate/chemosphere

Dioxin production during the thermal treatment of meat and bone meal residues

Juan A. Conesa *, Andres Fullana, Rafael Font

Department of Chemical Engineering, University of Alicante, Ap. 99, E-03080 Alicante, Spain

Received 20 October 2003; received in revised form 21 September 2004; accepted 23 September 2004

Abstract

Safe animal by-product disposal is a priority target as a result of the Bovine Spongiform Encephalopathy crisis in the European beef industry. One such disposal option is the incineration of by-product material such as meat and bone meal residues (MBM) for the purpose of energy recovery. Although currently applied, the thermal decomposition of MBM wastes has not been scientifically studied until now. A series of experiments has been performed to study the thermal behavior of MBM both in inert (N_2) and reactive atmosphere (air), both by thermogravimetry and in a horizontal laboratory furnace. As a general trend, MBM gives low PCDD/F values, compared with incineration of other wastes. Maximum yield of pollutants is observed at a nominal temperature between 700 and 800 °C.

Keywords: Pyrolysis; Combustion; Animal wastes; PCDD/F; Thermogravimetry

1. Introduction

Nowadays meat and bone meal (MBM) is being destroyed due to the possibility of being responsible for the transmission of the bovine spongiform encephalopathy (BSE), due to the presence of a protein species called 'prions', that cause Creutzfeldt-Jacob disease ('mad cows disease').

Import and export of MBM to/from/within the European Union has been banned since December 2000. Feeding MBM to cattle, sheep or goats has been banned within the European Union since July 1994.

The inactivation of the infection agent is very difficult. Only strong sodium hypochlorite treatment seems to achieve total inactivation. Germany proposed a process for the inactivation of the prions trough the use of destructive conditions (steam pressure > 3 bar; temperature > 133 °C; residence time > 20 min) and this process has been applied in many European countries, including Spain and Switzerland. The process however has many drawbacks, since these conditions destroy a major part of the infection agent, but not in totality. In many countries, brain and spinal cord (where large amounts of prions are concentrated) are removed and treated separately.

Dedicated incineration plants for MBM, as currently used in e.g., Belgium and England, only appear reasonable when sufficient quantities of MBM can be guaranteed in the long term. The most common technique is co-incineration, mainly in cement kilns. In the USA there are about 30 separate sites where cement kilns are burning hazardous waste derived fuel (US EPA, 1999).

* Corresponding author. Tel.: +34 965 903 400x2324; fax: +34 965 903 826.

E-mail address: ja.conesa@ua.es (J.A. Conesa).

0045-6535/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2004.09.089

From a thermal point of view, MBM is a good fuel (net calorific value approximately 17000 kJ kg^{-1}, similar to wood). It contains approximately 5% water, 22% ash, 40% carbon, 8% nitrogen, 6% hydrogen, 0.6% sulfur and 0.5% chloride, mainly as common salt. This composition however raises concerns about dioxin when incinerating this waste. Furthermore, MBM contains some metals (mainly copper, lead and chromine), known to act as catalysts in the PCDD/F synthesis reactions (Everaert and Baeyens, 2002).

The feeding rates in cement kilns vary from country to country. For example, in Spain the limit is 15% of the energy needed in the kilns, but there is no limit in Switzerland. Incineration of MBM and tallow is seen as useful by the cement industry, where the kiln offers good conditions for complete combustion in terms of temperature and time spent in the kiln. Substituting primary fossil fuels (coal or lignite) has moreover environmental and economic advantages (Scheuer, 2003).

Although industrially applied, the thermal decomposition of MBM wastes has not yet been scientifically studied in detail. Papers found in literature mainly deal with the reprocessing of the combustion residue. Knudsen et al. (2003) affirm that the reprocessing of the residual phosphate is difficult due to its high chloride content. Chaala and Roy (2003) suggest its use for agricultural soil enrichment in minerals and as a soil moisturizer. Deydier et al. (2003) evaluated the use of the combustion residue as a low cost substitute for materials in the process of lead sequestration from water effluents. Concerning the MBM combustion process, a paper has been found dealing with the behavior of MBM pellets in a fluidized bed combustor (McDonell et al., 2001). Beck et al. (2004) showed the effect of MBM co-combustion in a catalyzed reactor, showing an increase in catalyst activity. Other interesting effect in the co-combustion processes is the minimization of the emission of nitrogen compounds when bone meal is present (Goeran et al., 2002).

From a thermal point of view the solid phase undergoes two important steps in a combustion process: (i) a pyrolysis stage, which devolatilizes the solid feed to yield volatiles (gases and tars) and a solid char fraction; (ii) a combustion stage, involving heterogeneous reactions of the char to yield gaseous products and an inert residue (ash). The pyrolysis and combustion stages may be sequential or simultaneous, depending on the feature of the process considered (Conesa et al., 1998; Font et al., 2001).

The present work has two different and important parts in the study of the thermal decomposition of this material: (i) the thermogravimetric behavior of the MBM both in nitrogen and air atmospheres is presented; (ii) a series of experiments in a horizontal laboratory furnace has been performed including the analysis of the pollutants produced (mainly dioxins and furans).

2. Methods and materials

The material employed (MBM) was obtained from a cement plant situated close to our working center and owned by the CEMEX group. The plant requires 15 ton h^{-1} of coke and approximately 10% is replaced by MBM materials. Table 1 presents the analysis of the MBM sample, performed in a Carlo Erba Instrument (model CHNS-O EA110), and also chloride data obtained by X-ray fluorescence. As commented before, most of the chloride in MBM is present as common salt (NaCl). The MBM was well mixed in a mortar. The amount of fatty compounds (measured by extraction in a mixture 1:1 of dichloromethane: toluene for 24 h) is approximately 12 wt%. The net calorific value (16900 kJ kg^{-1}) was measured in a calorimetric bomb (Leco Instruments) (average of two measurements).

MBM has a brownish color, a bulk weight of 680 kg m^{-3} and an intense sweet odor. It should be noted that, if stored improperly in damp conditions, MBM provides an ideal medium for a variety of bacteria, fungi or vermin. The average particle size used in this study is 0.125 mm.

The thermogravimetric experiments were carried out in a Netzsch Thermobalance, model TG209 controlled by a PC system. The atmosphere used for pyrolysis was nitrogen and for combustion was synthetic air. The mass of the samples used was 10 mg approximately. Experiments were carried out with heating rates of 10, 20 and 30 K min^{-1} over a range of temperatures that included the entire range of solid decomposition, i.e., 80–800 °C.

The experiments of the second part of the study were conducted in a horizontal furnace shown in Fig. 1. The programmed temperature of the runs was varied between 600 and 1100 °C. Fig. 1 also shows a typical temperature profile of a combustion experiment (at 850 °C). In each experiment, 0.1 g of MBM was placed in the sample holder and combusted by introducing the sample holder inside the furnace at a specific velocity (0.46 mm s^{-1}) and maintained inside the furnace for 20 min. After passing through the furnace, the reactor gas was collected in an adsorptive trap containing XAD-2 resin. After each experiment, the adsorptive trap was extracted using toluene and the extract was analyzed using a High Resolution Gas Chromatography–High

Table 1
Analysis of the raw material

C	H	S	N	O[a]	Cl[b]
40.4	6.4	0.5	7.8	11.9	0.8
Moisture 3.5%		Ash 28.7%			

[a] By difference.
[b] Measured by X-ray fluorescence.