Waste Management xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Influence of pork and bone on product characteristics during the fast pyrolysis of pig carcasses

Yike Zhang, Zengyi Ma *, Jianhua Yan

State Key Lab of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China

ARTICLE INFO

Article history:
Received 28 December 2017
Revised 2 February 2018
Accepted 12 February 2018
Available online xxxx

Keywords:
Pyrolysis
Swine carcass
Meat
Bone
Mineral

ABSTRACT

The characteristics of the products of pig carcass pyrolysis depend on initial feedstock composition, specifically tissue and bone, as well as the interaction between these components. In this work, the raw pork (RP), pig bone (PB), and a mixture of RP and PB to simulate pig carcasses with a mass ratio of 2:1 (RB21) were pyrolyzed at 650 °C and compared to investigate pig carcass pyrolytic product characteristics. The presence of minerals in PB was found to increase the gaseous product yields of RB21 by 16%, especially the CO_2, C_2H_4 and C_2H_6 yields through steam gasification and steam reforming reactions. These minerals also affect tar product distribution, promoting the cracking of long chain hydrocarbons and the cyclization reaction of hydrocarbons, esters, amides/nitriles to produce more aromatic, O-heterocyclic and N-heterocyclic compounds, respectively. The Brunauer–Emmett–Teller (BET) surface area of pyrolytic RB21 char is 134.025 m^2/g and it is a porous material rich in minerals like Ca, P, and K. The addition of RP causes more wrinkles on the surface and reduces its mesopore diameter from 6.263 nm to 5.412 nm. The Ca and P in char are derived from hydroxyapatite occurring in PB, and K presents in RP participates in the crystallization of RB21 char, forming a new crystal compound $Ca_8H_2(PO_4)_6{\cdot}KHCO_3$.

1. Introduction

Routine or accidental death during livestock husbandry naturally produces a substantial amount of livestock carcasses. According to the Food and Agriculture Organization (FAO) (FAO, 2015), live animal production totals 4.85×10^9 animals every year including cattle, sheep, goats, pigs, and buffalo from livestock farms, and the mortality rate of these animals (3–5%) yields a total of 1.94×10^8. This value is even larger during outbreaks of infectious diseases like swine fever, foot-and-mouth disease (FMD) or Bovine Spongiform Encephalopathy (BSE) (Jori and Etter, 2016; Sánchez-Vizcaíno et al., 2013; Sugiura et al., 2014).

To dispose of livestock carcasses effectively and carefully, relevant methods including incineration (Staroń et al., 2017), rendering (Kalbasi-Ashtari et al., 2008), and composting (Xu et al. (2009)) have been developed, but they have defects, such as the emission of gas pollutants (i.e., incineration), by-product wastewater production (i.e., rendering), and long processing times (i.e., composting). Compared with the three methods mentioned before, pyrolysis represents a promising alternative as it can shorten processing times, destroy pathogenic bacteria, and produce bio-oil and syngas for further utilization (Hassan et al., 2016). However, related studies are rarely reported in recent literature (Gwyther et al., 2011).

Typically, for large-scale pyrolytic disposal of livestock carcasses in rotary kilns, the carcasses are frozen and then cut into pieces. In general, the carcasses are subjected to pyrolysis as a mixture of meat and bone, and the pyrolytic product characteristics arising from the carcasses are related to the pyrolytic characteristics of the meat and bone, and their interaction therein.

Several studies have been conducted on the pyrolytic products of bone, especially on charred bone. This is because the bone char and its derived materials have potential for utilization in fields such as soil amendment (Zwetsloot et al., 2015, 2016), electrochemistry (Wei et al., 2011), water purification (Iriarte-Velasco et al., 2015; Patel et al., 2015; Rojas-Mayorga et al., 2013, 2016) and archaeology (Kaal et al., 2016; Reidsma et al., 2016). With respect to studies on the pyrolysis of meat, several have focused on producing biodiesel due to its high fat content (Banković-Ilić et al., 2014; Chakraborty et al., 2014). As for mixtures of meat and bone (MBM), which represent the most similar materials to the carcass feedstocks discussed in this work, kinetic studies of MBM have shown that most of the organic matter is pyrolyzed from 200 °C to 600 °C, according to derivative thermogravimetric (DTG) curves (Ayllón et al., 2005; Conesa et al., 2003; Skodras

* Corresponding author.
E-mail address: mazy@zju.edu.cn (Z. Ma).

https://doi.org/10.1016/j.wasman.2018.02.025
0956-053X/

et al., 2007). Chaala and Roy (2003) studied vacuum pyrolysis of MBM at 500 °C and 15 °C/min, which generated valuable products including combustible gas, high calorific value pyrolytic oil, and solid residues rich in minerals. Ayllón et al. (2006) continued this research in a fixed bed reactor, revealing that final process temperature had a greater influence on the MBM pyrolysis process than the heating rate, and main products were tar and char under the conditions studied. Chemical analysis of tar components studied by Cascarosa et al. (2011) indicated that alkanes, alkenes, alcohols, and nitriles represent the main components in tar, and this tar can be converted to CO and H_2-rich gas through catalytic steam reforming over Ni/γ-Al_2O_3 catalysts (Lónyi et al., 2013). For char, Ren et al. (2011) conducted experiments to prove that MBM char has high gasification reactivity due to its high mineral contents.

However, the pyrolytic feedstock discussed in this work is different from typical MBM, as it represents a mixture of raw meat and bone, while MBM typically represents by-products from the rendering process, and most of its components are protein and bone (Kalbasi-Ashtari et al., 2008), which is a vital aspect of this work. To understand the pyrolytic characteristics of livestock carcass, more direct examination of mixtures of raw meat and bone from animal carcass should be implemented in research strategies. Therefore, in this work, using pig carcasses, this work characterizes pyrolysis of raw pork (RP) and pig bone (PB), and their combination thereof to represent livestock carcass and its components. To achieve this, RP was mixed with PB at a mass ratio of 2:1 to represent the pyrolytic feedstock, and this mixture is abbreviated as RB21 hereafter. Importantly the study of pyrolytic product distribution from RB21 can show the effect of interaction between RP and PB. Overall, the work here examines the pyrolytic characteristics of RP, PB and RB21 to provide reference for future pilot livestock furnace development and ensure a more sustainable process for the disposal and valorization of livestock carcasses.

2. Materials and methods

2.1. Sample preparation

Pork was chosen from the belly and back legs of pig carcasses, then diced and ground into powder under liquid N_2, to obtain homogeneous RP samples. PB samples were selected from pig carcass legs, wherein the PB samples were boiled in deionized water to remove the residual meat, and then dried at 105 °C in an oven for 24 h. Finally, after pretreatment, these PB samples were ground into powder, and collected and stored. RP and PB powders were then mixed at a mass ratio of 2:1 to obtain RB21. Detailed results of the proximate analysis and ultimate analysis of RP and PB are presented in Table 1.

Table 1
Proximate analysis, ultimate analysis and metal content analysis of RP and PB in air dried basis.

		RP	PB
Proximate analysis (wt.%)	Moisture	4.05	0.86
	Ash	1.52	39.30
	Volatile	90.94	57.29
	Fixed Carbon	3.49	2.55
Ultimate analysis (wt.%)	C	63.23	37.93
	H	9.80	5.39
	N	4.20	7.04
	S	0.58	0.20
	O[a]	16.62	9.27
Water content in as received basis		54.22	–
Metal content analysis[b] (wt.%)	Na	0.05	0.26
	P	0.18	7.97
	K	0.28	0.07
	Ca	0.01	14.84

[a] Calculated by difference.
[b] Analyzed by EDX.

2.2. Pyrolysis reactor

According to the design of a newly proposed pyrolytic rotary kiln, the pulverized carcasses were directly subjected to a high pyrolytic temperature, which is conducive to shortening the heat transfer time. The rotary nature of the kiln helps to increase the exposure of carcasses to that high temperature, so that the livestock carcass requires shorter pyrolysis processing times. To simulate the pyrolysis process in a rotary kiln, bench-scale fast pyrolysis experiments in a tubular furnace pre-set at 650 °C were performed as shown in Fig. 1. The pyrolysis temperature selected (650 °C) in this work was based on the operating temperature of future pyrolytic rotary kiln. Approximately 1 g of RP, PB and RB21 were placed in a crucible and directly subjected to pyrolysis for 10 min.

The carrier gas was N_2 with a flow rate of 100 mL/min (STP). During pyrolysis, pyrolytic products flowed through two scrubbing bottles filled with 150 mL cold dichloromethane. Pyrolytic tar was absorbed and then recovered through Soxhlet extraction at 50 °C and 850 mbar. To absorb water generated from pyrolysis process, analogous experiments were conducted but the absorption liquid in the scrubbing bottle was changed to alcohol, the water content in the pyrolytic products was measured by using a Karl–Fisher moisture titrator. The pyrolytic gas was collected after passing through the trap in a gas bag. After pyrolysis, the char in crucible was collected. The weights of obtained water, tar and char were measured, and the mass yield of gas was calculated using the difference between sample weight and the sum weight of water, pyrolytic tar and char.

2.3. Pyrolytic products analysis

Several methods were used to analyze pyrolytic product components. The gas components were determined by Agilent Technologies 490 Micro GC combined with a thermal conductivity detector (TCD). Two different columns were used to detected different types of gas components. Specifically, H_2, CH_4 and CO were identified by an MS5A (10 m) column with Ar as the carrier gas, and CO_2, C_2H_4 and C_2H_6 were identified by a PPU (10 m) column with He as the carrier gas. The injector temperature and column temperature for both columns were 60 °C and 80 °C, respectively. The running time for detection was set at 4 min.

The composition of the resultant pyrolytic tar was determined by DSQ- II GC/MS (Finnigan, America). For GC analysis, the DB-WAX capillary column (30 m-0.25 nm-0.25 μm) was used with the oven temperature initially held at 120 °C for 5 min, then elevated to 240 °C at a rate of 5 °C/min, and finally held at 240 °C for 15 min. The injector temperature was set at 250 °C with He as the carrier gas at a flow rate of 1 mL/min. The full-scan mode under electron ionization (70 eV) with a m/z ratio from 35 to 450 was used for MS. The tar compounds were identified accordingly using the NIST database.

X-ray Diffraction (XRD) was performed on a PANalytical X'Pert PRO (Netherlands) with Cu-Kα radiation using a generator voltage of 40 kV. The measurements were collected in the range from 10° to 80°, with a 2θ step count of 0.02° and a step time of 5 s.

The textural parameters of char samples were measured by an AUTOSORB-IQ2-MP instrument (Quantachrome, America) using N_2 adsorption at 77.35 K. Before analysis, the char samples were outgassed in a vacuum at 120 °C for 24 h. The pore size distribution and pore volume of the micropore (<2 nm) were evaluated by DFT model (assuming slit/cylindrical pores) (Guizani et al., 2016; Iriarte-Velasco et al., 2015), while mesopore (2–50 nm) and

Please cite this article in press as: Zhang, Y., et al. Influence of pork and bone on product characteristics during the fast pyrolysis of pig carcasses. Waste Management (2018), https://doi.org/10.1016/j.wasman.2018.02.025