Fuel Processing Technology 171 (2018) 45–53

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Research article

Effect of water, fat, and protein in raw pork from swine carcasses on the pyrolytic gaseous and liquid product distribution

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ARTICLE INFO

Keywords:
Pyrolysis
Livestock carcass
Moisture
Lipid
Protein

ABSTRACT

Pyrolysis is an effective way to dispose livestock carcasses. Pork is selected as meat from a representative carcass and the effect of its components (water, fat and protein) on the gaseous and liquid pyrolytic product distribution is investigated. Water has a significant influence on the amount of gaseous products formed, and its presence in raw pork (RP) leads to greater CO, H_2, and CH_4 yields through the steam gasification and steam reforming reactions. In addition, the presence of water results in higher conversion of N containing compounds into NH_3, rather than HCN. Tar yields were mostly determined by the products obtained from the pyrolysis of fat, which include compounds derived from the cracking, decarboxylation, and decarbonylation of long chain fatty acids. The decomposition of protein led to the formation of small molecules like NH_3, HCN, and phenols. In addition, protein and fat pyrolysis products react to form long chain amides and nitriles, increasing the tar yield. More toxic heterocyclic compounds are obtained in pyrolytic tar through the cyclisation of long chain hydrocarbons and nitriles under higher temperatures.

1. Introduction

Livestock carcasses represent an important waste in the livestock industry. With livestock production becoming larger and more concentrated, the safe and effective disposal of livestock carcasses as a result of routine or accidental death during one of the stages in livestock growth is becoming a more important consideration. With so many farms around the world breeding approximately 4.85×10^9 livestock (e.g. cattle, sheep, goats, and pigs) in 2015 [1], about 1.94×10^8 animal carcasses need to be disposed environmentally and safely (the mortality of livestock is about 3–5%). One incident where thousands of pig carcasses were found floating in the Huangpu river of Shanghai (China) in 2013, resulted in serious water pollution [2], and drew public attention to the importance of proper livestock carcass disposal.

Methods to dispose these carcasses include incineration, rendering, and composting. As for incineration, Staroń et al. [3,4] conducted experiments to incinerate meat industry waste, producing ashes with macro- and micronutrients that can be used as additives for fertilizer. But the incineration process generates gas pollutant such as NOx and polycyclic aromatic hydrocarbons [5]. For rendering, as the by-products after the rendering of carcass, meat and bone meal can be co-combusted with coal to reduce the coal consumption [6]. However, the waste water after the rendering process is difficult to handle properly. The composting is mostly used by farmers to improve soil fertility, yet it takes a lot of time to convert carcass and animal waste to useful fertilizer, and it may cause water pollution and greenhouse gas emissions [7].

To avoid defects of the three methods mentioned before, in this work, a promising method to dispose carcasses safely and effectively is via pyrolysis due to its short processing time, and the high temperatures required which can eliminate pathogenic bacteria. Importantly, pyrolysis can generate bio-oil and bio-gas as a renewable energy source [8]. However, there are few studies on the pyrolysis of livestock carcasses, as a new feedstock for bio fuel production [9].

The main components in livestock carcasses are water, fat, and protein, with water being the principal component. According to previous studies, pyrolysis of moisture-rich biomass consists of two main processes: the evaporation of water from the wet biomass, followed by pyrolysis of the dried biomass [10,11]. The water of the pyrolyzed biomass affects the tar content [12,13], the gas composition [13–16], and the char characteristics [15–17]. Animal fat has been found to be a good substrate for producing biodiesel via pyrolysis [17–21]. Researchers Ben Hassen-Trabelsi et al. [22] and Kraiem et al. [23] showed that after pyrolysis of waste animals fats, the ensuing oil consisted of a mixture of hydrocarbons, carboxylic acids, aldehydes, ketones, esters, and other minor components. The type of components present in bio-oil are highly dependent on the chemical structure of the triglycerides

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https://doi.org/10.1016/j.fuproc.2017.10.020
Received 15 August 2017; Received in revised form 20 October 2017; Accepted 30 October 2017

present in the animal fat [24,25]. As a high nitrogen content material, protein can generate various products including NH_3 and HCN in the gaseous state [26], as well as nitriles, amides/amines, oximes, and heterocyclic compounds in the liquid state through various processes such as deamination, decarboxylation, cyclisation, and dehydration [26–30]. The reaction pathway determining the composition of the pyrolytic products can be affected by factors such as temperature [21], the kind of unreactive carrier gas [32], and even the kind of inorganic species present in the animal matter [33].

However, the interactions among water, fat and protein in samples directly obtained from animal carcasses cannot be neglected. In Wang's work [34], castor oil and soybean protein were selected as representative examples of animal fat and protein respectively. The interaction between these two components produced a protein-fatty acid condensate surfactant, but this interaction had little effect on the bio-oil yield. Nevertheless, the difference in terms of pyrolysis products obtained between these two model fat/protein surrogates and fat/protein found in real animal samples cannot be neglected. A more realistic investigation would involve pyrolysis of an animal carcass containing the exact kind and content of fat/protein found in nature such as that found in raw carcasses.

Hence, in this work we have chosen a pig carcass as a representative example of a typical livestock carcass, and have studied the product distribution from the pyrolysis of raw pork (RP) and freeze-dried pork (FDP). Fat and protein were further extracted from the FDP, and the level of their interaction in FDP was determined by studying their pyrolytic product distribution. The effect of the carcasses' water content on the pyrolytic product distribution is also considered. Accordingly, an analysis of the gas and tar components obtained after pyrolysis of RP can serve as a reference for the design of future livestock pyrolytic rotary kiln. Moreover, the char products of RP will be studied together with the char products after pyrolysis of pig bone, thus the detailed discussion of char products is beyond the scope of this work.

2. Materials and methods

2.1. Sample preparation

Streaky pork was selected from the dead pig's belly and back legs, then diced and stored at − 80 °C to prevent decomposition. Afterwards, it was ground into a powder under liquid N_2 to obtain a homogeneous RP sample. The liquid N_2 was used to freeze and trap any moisture and to harden the sample, making it easy to grind.

The RP was freeze dried under vacuum with a freezing dryer at − 25 °C, 0.63 mbar for 24 h to remove moisture, thus forming FDP. Drying under low temperature helps to protect the protein structure and reduce the volatility of small molecules.

Fat was extracted from the FDP by Soxhlet extraction. Hexane solvent (150 mL) was used per 2 g FDP and the extraction processing temperature was kept at 70 °C for 12 h. After the extraction process was finished, the solvent was removed under reduced pressure via rotary evaporation (50 °C, 370 mbar). The amount of fat collected was then weighed.

Protein was extracted from FDP through the trichloroacetic acid (TCA)/acetone precipitation procedure reported by Wu et al. [35]. FDP (0.04 g) was dissolved in 1.5 mL of TCA/acetone solution (10% TCA wt/vol in acetone) at − 20 °C, with 0.01 mol/L dithiothreitol (DTT) being added just before the dissolution of FDP; the mixture was then allowed to stand for 1 h. The solution was centrifuged at 15000 × *g* for 5 min at 4 °C, and the precipitate was collected. Dissolution and centrifugation were repeated until the precipitate was fully white. Finally, the precipitate was washed three times with 1.5 mL of cold acetone and centrifuged it at 15000 × *g* for 5 min at 4 °C. The final precipitate was air-dried, thus obtaining a dried, purified protein sample.

Quintuplicate extraction processes for RP, fat, and protein were performed. The mean of these 5 experiments were treated as the content of each component for the purposes of this work. Detailed results including proximate analysis, calorific values, and ultimate analysis are presented in Table 1.

Table 1
Component analysis and corresponding proximate analysis, calorific values, and ultimate analysis of RP, FDP, fat, and protein.

		RP	FDP	Fat	Protein
Component analysis[a] (wt%)	Water	54.22	–	–	–
	Fat	29.20	63.79	100.00[d]	–
	Protein	15.58	34.03	–	100.00[d]
Proximate analysis[a] (wt%)	Moisture	54.22	0.17	0.01	0.46
	Ash	0.72	1.58	0.03	4.61
	Volatile	43.39	94.62	99.92	86.67
	Fixed carbon	1.66	3.63	0.04	8.26
Ultimate analysis[a] (wt%)	C	30.17	65.79	73.24	48.13
	H	4.68	10.20	11.61	7.00
	N	2.00	4.37	1.32	11.39
	S	0.28	0.60	0.14	1.14
	O[b]	7.93	17.29	13.65	27.27
Water content[c] (wt%)		4.05	0.15	0.01	0.37
Gross calorific value[c] (J/g)		32,887	32,963	38,332	20,633

[a] In as received basis.
[b] Calculated by difference.
[c] In air dried basis.
[d] Assume that the sample is clear from impurities.

2.2. Pyrolysis set-up

In our future large-scale disposal of livestock pyrolytic in rotary kiln, carcasses are cut into small pieces before subjected to pyrolysis. The small size of carcasses reduces the heat transfer time, and the rotation of rotary kiln increases the exposure of carcasses to high temperature, thus making fast pyrolysis condition possible. To match the pyrolytic condition in the furnace, five parallel fast pyrolysis experiments were carried out in a tubular furnace with the pyrolysis temperature pre-set as an increase from 500 °C to 700 °C, via 50 °C increases at specific intervals. Nitrogen was selected as the carrier gas at a constant flow rate of 100 mL/min. The sample was placed in a crucible (1 g), and held in a reactor for 10 min. As shown in Fig. 1 (by-pass A), the pyrolytic tar was absorbed in a trap that consisted of two scrubbing bottles filled with 150 mL cold dichloromethane. Afterwards, the trapped tar was recovered by removing the solvent under reduced pressure (50 °C, 850 mbar), and its content was weighed. The pyrolytic gas was collected after flowing through the tar trap in a gas bag. After each experiment, the remaining char in the crucible was collected and weighed. The mass yield of gas was calculated using the difference between initial weight of feedstock and the recorded combined weights of liquid and char products. Analogous tests were conducted with RP and FDP but the absorption liquid was changed to alcohol in order to absorb water evaporated from RP and FDP. The amount of water collected in the alcohol trap was measured with a Karl-Fisher moisture titrator.

2.3. Gas chromatography (GC)

The gaseous products collected in the gas bag were assessed with an Agilent Technologies 490 Micro GC using a thermal conductivity detector (TCD). Two different columns were used based on the type of analyte being detected. The MS5A (10 m) column was used to identify H_2, CH_4, and CO using argon as a carrier gas; the PPU column (10 M) was used for identifying CO_2, C_2H_4, and C_2H_6 using helium as a carrier gas. The injector temperature was set at 60 °C and the column temperature was set at 80 °C, with a running time of 4 min.