

PYROLYSIS STUDY ON CATTLE MANURE: FROM CONVENTIONAL ANALYTICAL METHOD TO ONLINE STUDY OF PYROLYSIS PHOTOIONIZATION TIME-OF-LIGHT MASS SPECTROMETRY

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ABSTRACT

The pyrolysis behavior of cattle manure was analyzed by three methods in this work: thermogravimetric analyzer (TG), Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) and pyrolysis photoionization time-of-light mass spectrometry (Py-PI-TOFMS). The pyrolysis process of cattle manure could be divided into four stages, dehydration stage, lignocellulose decomposition stage, lignin and protein decomposition stage, char and mineral matter decomposition stage. The products was mainly classified into six groups: ketones, aldehydes, phenolic compounds, acids, hydrocarbons and N-containing compounds. Based on the time-evolved profiles and temperature-evolved profiles, the characteristics of these major products were analyzed and discussed. Furthermore, their possible formation pathways were also proposed and discussed.

Keywords: Cattle manure, Pyrolysis, Products analysis, TG, GC-MS, PI-TOFMS

1. INTRODUCTION

As one of the most abundant biomass sources in China, over 2.6 billion tons of fresh livestock manure are produced every year. However, its multipurpose utilization rates at present is only 0.9% and the excessive manure produced by feeding industry may cause serious environmental and food safety problems[1]. One of the potential ways to tackle these problem is to convert livestock manures into biofuels and value-added products by thermochemical conversion method. Since pyrolysis is the fundamental of thermochemical conversion processes, a better understanding of its behaviors and mechanisms is needed to utilize livestock manures efficiently.

Previous studies were mainly focus on the identities of pyrolysis products rather than then mechanism analysis. Furthermore, due to the lack of observation of

internal pyrolysis products, it was difficult to have a description on the process of livestock pyrolysis. The aim of this work was to investigate the thermal decomposition behaviors of cattle manure using by thermogravimetric analyzer (TG), (Pyrolysis-gas chromatography/mass spectrometry) Py-GC/MS and pyrolysis photoionization time-of-light mass spectrometry (Py-PI-TOFMS) technology. The weight loss of feedstock and mass spectra of typical products could be obtained to elucidate the primary decomposition pathway of cattle manure pyrolysis.

2. MATERIAL AND METHODS

2.1 Material analysis

Cattle manure, as a typical livestock manure, were collected from a local farm in Tianjin, China. After air drying, the cattle manure sample was ground into particles of 0.2-0.3 mm size for experiments. Its proximate analysis and ultimate analysis were shown in Table1. Prior to the experiments, the samples were put into an oven at 105°C for 24 hours to lower the water content.

2.2 Thermogravimetric experiments

Pyrolysis tests were carried out in a differential thermogravimetric analyzer (Q500, TA, USA), which was able to provide a continuous measurement of weight loss as a function of time or temperature. In this experiment, 10 mg samples were held at 100°C for 10 min to remove the moisture and then heated to 900°C at the heating rate of 5°C/min under Nitrogen with a flow rate of 30 ml/min.

2.3 Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) experiments

Py-GC/MS analysis was performed on a CDS Pyroprobe 5000 Series pyrolyser connected to a gas

Table 1. The basic analysis of cattle manure samples

Proximate analysis (wt.%)		Ultimate analysis(wt.%)		Component analysis (wt.%)	
Moisture	6.75	C	30.96	Cellulose	12.84
Volatile matter	52.96	H	2.34	Hemicelluloses	0.04
Fixed carbon	5.41	O ^a	63.62	Lignin	18.28
Ash	34.88	N	2.67	Crude fats	0.80
HHV (MJ/kg)	12.01	S	0.41	Crude proteins	16.78

^a By the difference

chromatography/mass spectrometry (GCMS-QP2010 SE, Shimadzu, Japan). In each experiment, 2 mg cattle manure was placed in a quartz filler and pyrolyzed at a series fixed temperature (300, 400, 500 and 600°C) with a reaction time of 20s. the pyrolysis products were separated in a capillary column of Porapak Q column and 5A molecular sieve. In order to prevent the condensation of products, the sample injection temperature was maintained at 300°C.

2.4 Pyrolysis photoionization time-of-flight mass spectrometry (Py-PI-TOFMS) experiments

The Py-PI-TOFMS experiments were performed in the national synchrotron radiation laboratory in Hefei, Anhui, China. The experiments were carried out using a homemade Py-PI-TOFMS apparatus that consists of a tubular furnace, a transfer line and a mass spectrometer. The tubular furnace was heated by electrical resistance, the temperature of which was controlled by a temperature controller (SKY Technology Development Co., Ltd., China) and measured by a K-type thermocouple. The system was purged with nitrogen for 15 min maintained at 200 SCCM. There are two experimental modes: 1) The furnace was hold at fixed isothermal conditions of 300, 400, 500 and 600°C. When the temperature reached the set value, the sample was introduced into the middle position of the furnace by a quartz sample boat. The spectra were recorded continuously for 1000s with 4s intervals and time-evolved profiles was obtained. 2) The temperature of sample increased from 30°C to 600°C at the heating rate of 5°C/min and spectra were recorded every 4s.

The pyrolysis products were transferred into the photoionization chamber and ionized by ultraviolet light emitted from a Kr lamp with a photon energy of 10.4 eV (PKS106, Heraeus, Ltd.,Germany). The ions were detected by TOF MS.

3. RESULTS AND DISCUSSION

3.1 TG and DTG analyses

The TG and DTG curves of cattle manure in Fig. 1 exhibited four stages during the thermal decomposition process at the heating rate of 5°C/min.

The first stage was the dehydration stage, roughly from room temperature to 200°C and with the weight loss of around 5% of original sample weight. The second stage was from 200°C to 450°C. Around 30% loss of the original weight was observed in this stage and the maximum weight loss rate was 0.29 wt.%/°C at 328°C. The weight loss during this stage was attributed to the lignocellulose decomposition and glucoside linkage scission. The weight loss rate of the third stage (450°C to 660°C) kept around 0.055 wt.%/°C. The weight loss for the third stage was around 15%, mainly resulting from the decomposition of lignin and protein. The 10% weight loss at the last stage may be due to the decomposition of lignin, char and mineral matter, and the peaks in DTG curves at this stage might be from the dehydration or calcination of mineral matters and the devolatilization of char.

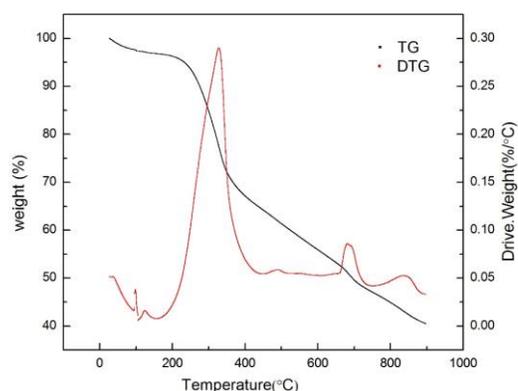


Fig 1 Thermogravimetric curves in cattle manure pyrolysis at the heating rate of 5°C/min

3.2 Py-GC/MS analysis

Py-GC/MS experiments were carried out at fixed isothermal conditions from 300°C to 600°C. As shown in Fig 2, the main organic products derived from cattle manure pyrolysis can be classified into ketones,

aldehydes, phenolic compounds, acids, hydrocarbons and N-containing compounds.

Ketones and aldehyde compounds, both derived from the breakdown of single sugar ring, were the major products of cattle manure pyrolysis and occupied 50% of the total products. The type and content of aldehydes decreased obviously when the temperature was over 400°C, which could be due to the possible secondary cracking and unsaturated bonds condensation. As opposed to aldehydes, the proportion of ketones increased sharply at 400°C and got its maximum at 500°C because high temperature was favorable for the decomposition of sugar units and the recombination of the opened bonds as well as some aldehydes converting into ketones. The content of phenolic compounds got its peak at 400°C and then decreased with the temperature further increasing because the demethoxylation and alkylation of phenolic compounds will be enhanced and decompose to small molecular chemicals or gas. Phenol and its derivative cresol were the most abundant type in phenolic compounds which indicated that the p-hydroxyphenyl unit was the major lignin structure of cattle manure. Hydrocarbons, mainly including aromatics and chain hydrocarbons were also detected in the pyrolysis process. Toluene was the major product in hydrocarbons and was mainly generated from the intermediate of anisole. Hydrocarbons were unstable at high temperature and there was a significant reduction from 31.8% at 300°C to only 13.6% at 400°C. N-containing compounds were the typical products of cattle manure pyrolysis, mainly including pyrrole, 1-methyl-1H-Pyrrole, Methyl-Pyrazine, 3,5-Dimethylpyrazole, indole and some nitriles. For cattle

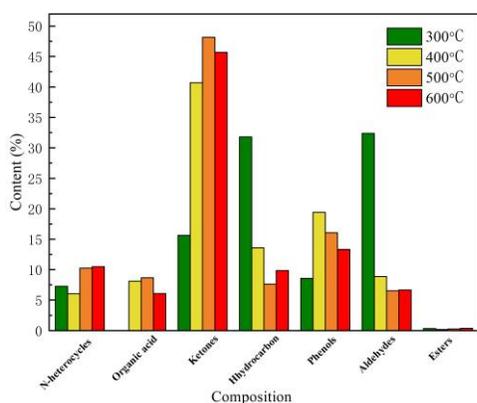


Fig 2 Effects of the reaction temperature on the major products in cattle manure pyrolysis

manure, amino acids were easy to react with sugars via the so-called Maillard reaction, leading to the formation of abundant N-Heterocycle compounds. In addition,

some NH₃ and amines could form N-heterocycles and nitriles by polymerization and cyclization.

3.3 Py-PI-TOFMS analysis

The effects of pyrolysis temperatures on the products distribution can be obtained by the mass spectra analysis. The mass spectra of products of cattle manure pyrolysis at different temperatures (300-600 °C) are presented in Fig. 3. Over a hundred products have been detected and can be grouped into several categories, i.e., alkanes (e.g., m/z 58 and 72), alkenes (e.g., m/z 42, 56), aromatics (e.g., m/z 92), phenols (e.g., m/z 94, 108, 124, 138, 152, 154, 164 and 194), ketones (e.g., m/z 48, 74, 82, 84, 96, 110, 112, 114, 126, 150, 180), aldehydes (e.g., m/z 98 and 100), acids (e.g., m/z 60) and nitrogen containing compounds (e.g., m/z 17, 67, 81, 97, 117). It shows that the signal intensities of most compounds significantly increased from 300°C to 400°C and then increased slightly with temperature increasing. It was due to the peak of weight loss rate ended at around 400°C where most compositions could be decomposed.

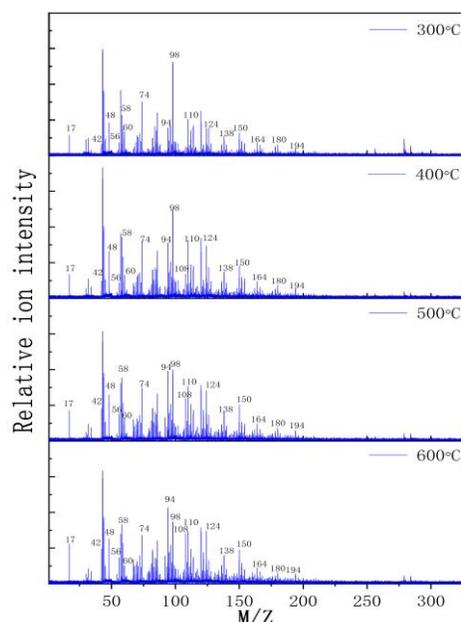


Fig 3 Mass spectra with the photo energy of 10.4 eV at different temperatures in cattle manure pyrolysis.

With the increase of temperature, the reaction time could also be shortened due to the acceleration of chemical bonds breaking, cyclization and polymerization. Fig. 4 showed the time-evolved profiles from the pyrolysis products of cattle manure at 500°C. As illustrated in Figs. 4 (a)-(c), aldehydes, ketones and acids were the major products of hemicellulose and cellulose pyrolysis. 2-methyl-pentanal (m/z 98) and 3-ethyl-2-pentanone (m/z 114) were first generated in cattle

manure pyrolysis, which could be considered as the primary products of hemicellulose and cellulose. Almost at the same time, they would be decomposed into smaller molecules like acetone (m/z 48) and 1-hydroxy-2-propanone (m/z 74). However, the generation of cyclopentenones and furanones was relative later, which means cyclization was more difficult than decomposition. In addition, several acetophenones (m/z 150,180) produced from lignin were also detected. In comparison with 4-Hydroxy-3-methylacetophenone, 3,5-Dimethoxyacetophenone needed more time to form because of the dihydroxylation reactions. Hydrocarbons might be from the decomposition of cellulose, protein and lipid. The generations of alkenes were much less and later than alkanes, but lasted longer time. The initial generation time of phenol (m/z 94) was earlier than that of 2-methoxy-phenol (m/z 124) and 2,6-dimethoxy-phenol (m/z 154), deducing that lignin with guaiacyl units and syringyl units were harder to decompose.

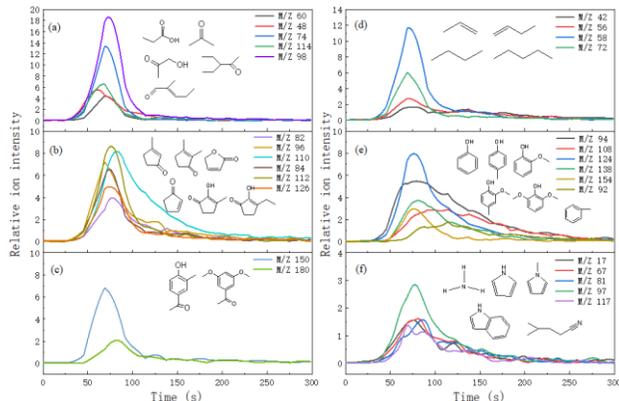


Fig 4 The time-evolved profiles from the pyrolysis products of cattle manure at 500°C

The formation temperatures of different products in pyrolysis process were also obtained from the temperature-programmed experiments and shown in Fig 5. Most products were generated between 200°C to 550°C which was consistent with the TG results. Consistent with the time-evolved profiles, the monosaccharide rings began to be cracked around 180°C and thereby forming some c-c chain structures, such as, 2-methyl-Pentanal and 3-ethyl-2-Pentanone. As the reaction went on, these chain structures could be broken down directly to form acids or ketones with 2 or 3 C atoms. Acetic acid began to form at around 230°C, indicating that the removal of the carbonyl and O-methyl required more energy. In terms of hydrocarbons, alkenes required higher temperature than alkanes, since they might be produced by the breaking of C-H bonds in alkanes. In addition, alkenes showed the another peaks

respectively at around 450°C which due to the secondary cracking of long chain hydrocarbons. As shown in Fig5(e), the formation of phenols with methoxyl needed higher temperature. The peaks of phenol, cresol and toluene appeared between 350°C and 400°C mainly due to the removal of methoxyl. NH_3 was generated from 200°C to 600°C, which indicated the temperature range of amino acids decomposition was wider than other compositions.

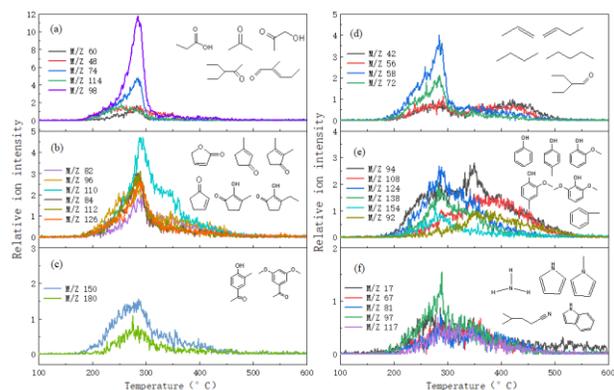


Fig 5 The temperature-evolved profiles from the pyrolysis products of cattle manure

4. CONCLUSION

The pyrolysis process of cattle manure was analyzed by TG, Py-GC/MS and Py-PI-TOFMS. The TG and DTG curves exhibited four stages during the thermal decomposition process of cattle manure. The pyrolysis products can be mainly classified into six groups: ketones, aldehydes, phenolic compounds, acids, hydrocarbons and N-containing compounds. More details of cattle manure pyrolysis were revealed by the time-evolved profiles and temperature-evolved profiles. The possible reaction pathway of characteristic products had also been discussed.

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