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Co-pyrolysis characters between combustible solid waste and paper mill sludge by TG-FTIR and Py-GC/MS

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ABSTRACT

In this work, the types of products and their proportions, the evolution characteristics of the functional groups and gases products, the pollutants emission of combustible solid waste (CSW), paper mill sludge (PMS) and their blends were investigated by Py-GC/MS and TG-FTIR. For the blends, the proportions of PMS were 10%, 30% and 50%. The percentage of pyrolysis products (acid, hydrocarbon, aldehyde, alcohol, benzene, furan, phenol, ester and ketone) was pointed out. Among these, the content of acid was the maximum. Blended with 10% PMS, the percentage of alcohol reached the greatest. Both single sample and blends could be divided into two decomposition phases. The residue mass of blends increased from 17.74% to 30.47% with the PMS ratio increased. O—H, C—H, C=O, C—O, SO_2, NO, HCl, CO, CH_4 and CO_2 were the main functional groups and gases products surveyed from the FTIR spectrums during co-pyrolysis. Adding PMS into CSW could reduce the emission of the pollutants and the lowest yield of pollutants (SO_2, NO, HCl, CO and CO_2) would be obtained covered with 50% PMS.

1. Introduction

The growth of social and the human's living standards, a large amount of energy has been consumed and the shortage traditional fossil fuel does not satisfy the demands for the development [1]. Biomass is considered as an optimal substitute for fossil fuels because of its renewable and environmental friendly. Combustible solid waste (CSW) is a complex mixture containing many combustible substances, such as paper, fruit and kitchen waste, branches [2]. The national amount of CSW reached 180 and 210 million tons in 2010 and 2015, respectively [3]. Paper mill sludge (PMS) is the primary waste residue after papermaking wastewater treatment in paper mill. Without useful and effective disposals to discharge, it will develop into a new large pollution source and the amount ran up to 0.26 Gt/a in 2012 [4,5]. Lower organic matter is the principal component of PMS, which are named as humic acid, amino acid, polycyclic aromatic hydrocarbon and so on. Traditional waste disposal methods, as it did in the case of landfills, face many problems. Land shortage and underground water pollution are the main problems. In recent years, the technology of pyrolysis waste has been applied to form bio-oil and bio-char frequently [6].

Among the various ways of biomass-energy use, co-combustion [7], co-pyrolysis [8] and co-gasification [9] these methods are applied for co-utilization of biomass. Pyrolysis, the thermal destruction lack of oxygen, is one of the most significant thermal conversion processed. The char, liquid and gas productions would came into being, which could be used as bio-energy. [10]. Thermogravimetric analysis (TGA) is a frequently-used technique to investigate the thermal events. Combined with thermogravimetry and Fourier transform infrared spectrometry (TG-FTIR), the species released from the thermal decomposition can be dynamically recorded [11]. Based on the application of measurements, the dynamical qualitative and quantitative characters of the materials and supplies are probable to achieved [12]. The pyrolysis gas chromatography/mass spectrometry (Py-GC/MS) is proven to be a fast instrument for separating and identifying the volatile products yield from the decomposition process [13]. Curious about the chemical structures and the products of biomass, many previous works had been done to study the evolution of functional groups, and the quantity and quality of pyrolysis products. Oudghiri [12] researched the TG-FTIR analysis on pyrolysis and combustion of marine sediment. Biller [14] determined the biochemical composition of microalgae through GC/MS. The team of Miandad [15–17] studied the pyrolysis liquid oil of plastic waste with or without catalytic using FT-IR and GC–MS. PS plastic waste showed maximum production of liquid oil (80.8%) with gases 13%. After using

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Nomenclature

CSW	combustible solid waste
PMS	paper mill sludge
Py-GC/MS	pyrolysis gas chromatography/mass spectrometry
TG-FTIR	thermogravimetry/Fourier transform infrared spectroscopy
PVC	polyvinyl chloride
SO_2	sulfur dioxide
CO_2	carbon dioxide
CO	carbon monoxide
NO	nitric oxide
HCl	hydrogen chloride
CH_4	methane
Cl	chlorine
N	nitrogen
S	sulfur
T_i	the initial temperature
T_f	the terminal temperature
M_f	the pyrolysis residue mass
DTG_1, DTG_2	the mass loss rate according to the first peak and the second peak
T_1, T_2	the temperature according to the first peak and the second peak

synthetic and natural zeolite, the liquid oil yield decreased to 52% and the gases increased to 17.7%. However, the quality of the pyrolysis liquid oil has been improved. Although there were a lot of researches for biomass using TG-FTIR and Py-GC/MS, including researches for waste, the paper on co-pyrolysis CSW and PMS was less found. At the same time, CSW and PMS were the pollution of waste, urgently needed to be solved. In addition, experiments showed that there were some advantages about co-utilization of CSW and PMS. Interactions generated in the process and it became more obvious at high temperature [7]. Adding PMS into CSW could also reduce the activated energy [5]. Therefore, co-pyrolysis CSW and PMS was a significative work.

Py-GC/MS and TG-FTIR were used in this paper to explore the characters of co-pyrolysis of CSW and PMS. This study was noteworthy. The types of products and their proportion, the functional groups and gases products changed in the process, and the emission of pollutants with different mixing ratios were studied in this paper.

2. Materials and methods

2.1. Materials

In a paper mill in Guangdong Province China, the paper mill sludge (PMS) was gained. The combustible solid waste (CSW) was a complex mixture. The contents of the main components in CSW were listed in Table 1 [2]. According to GB/T212-2008, GB211-84 and ASTM D5373-08 these standards, the ultimate analysis and proximate analysis of CSW and PMS were measured, and displayed in Table 2. As for the formal researches [5,18], the ratios 0%, 10%, 30% and 50% of PMS were suitable which were named as 100CSW, 90CSW10PMS, 70CSW30PMS and 50CSW50PMS. Some pre-treatments of CSW and PMS needed to be done before the experiments. Firstly, the samples were dried at 105 °C for 24 h in an oven. Then crushed and sieved the uniform particle size, less than 178 μm. Finally, after the CSW and PMS mixed in proportion, the materials were placed in the dry dish for the following experiments.

Table 1
Composition of CSW on as received basis (wt%).

Component	Food and fruit waste	Wood	Paper	PVC
CSW	46.4	4.7	18.2	30.7

2.2. Experimental facility and methods

In this study, the thermogravimetric simultaneous thermal analyzer (METTLER TOLEDO TGA/DSC1) was examined for co-pyrolysis. The pyrolysis process were studied at N_2 atmosphere with a flow rate of 80 ml/min and the temperature range was 110–900 °C. For consistent comparison, the amount of samples was 5 ± 0.2 mg for each experiment. The heating rate of all the tests was 30 °C/min and all the experiments were repeated to guarantee the correctness.

The Fourier transform infrared measurements (Nicolet™ iS™ 10 FT-IR spectrometer) was used to identify the gas emission products from the co-pyrolysis process. In order to avoid the gas condensation, the volatiles from TG into FTIR, passed through a heated line, which maintained at 215 °C. Then FTIR spectra in the range 4000–400 cm^{-1} IR absorption band to 4 cm^{-1} resolution were collected and stored for further processing.

The fast pyrolysis analyzer (CDS5200) was coupled with gas chromatography/mass spectrometry (Aglien 7890BGC, 5977AMS) systems to research the distribution of volatiles from samples fast pyrolysis against reaction temperature. About 2 ± 0.1 mg of sample was loaded in the pyrolysis tube in the N_2 atmosphere and the residence time for samples was 20 s. The flash heating rate was set to 20 °C/ms and the pyrolysis temperature of the furnace was 800 °C. Then, the volatiles were detected by GC/MS. The injector temperature kept at 300 °C and the chromatographic separation was performed with a HP-5 ms (30 m × 250 μm × 0.25 μm). With the heating rate of 10 °C/min, the temperature of the chromatographic column raised from 50 °C (2.25 min) to 300 °C (5 min). On the basis of NIST library and some previous reports, the yields of the compounds could be determined by GC/MS.

3. Results and discussions

3.1. Py-GC/MS analysis for pyrolysis of CSW and PMS

In order to obtain a better insight into the formation of volatile organic compounds, Py-GC/MS analysis on the co-pyrolysis of com-

Table 2
The ultimate analyses and proximate analyses of CSW and PMS on dry basis.

Samples	Ultimate analyses (wt%)					Proximate analyses (wt%)		
	C	H	O	N	S	Volatile	Fixed carbon	Ash
CSW	45.28	6.14	39.47	1.28	0.23	77.52	14.88	7.60
PMS	16.46	1.63	20.22	0.7	1.42	39.16	1.27	59.57