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A study on co-pyrolysis of bagasse and sewage sludge using TG-FTIR and Py-GC/MS

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ABSTRACT

In this paper, the pyrolysis process of mixed samples, bagasse with the addition of sludge, were investigated by TG-FTIR, and Py-GC/MS. For the mixed samples, the proportions of sludge were 10%, 30% and 50%. With the sludge ratio increased, the initial temperature and the terminated temperature increased. Eleven chemical structure groups were resolved from both of bagasse and sludge by KBr-Tabletting based FTIR analysis. Aromatic compounds, CO_2, C═O, C─O, NH_3 and HCN were the major gaseous products surveyed from the TG-FTIR inspection. The percentage of pyrolysis products (acetic acid, $C7_{\#}$, furfural, benzene derivatives, $C7_P$) were figured out from Py-GC/MS analysis. The addition of sludge was beneficial for the production of group $C7_P$, whose carbon atoms exceeded 7. This research provided useful background knowledge for co-pyrolysis of bagasse and sewage sludge.

1. Introduction

A great number of sewage sludge is produced with the dramatic growing of municipal wastewater treatment plant. As reported in China, at least 11.2 M tons of dry sewage sludge is generated by thousands of wastewater treatment plant, and the growth rate is 10% a year [1]. Some researches had found that approximate 50% weight of sewage sludge was organic content, most of which were hemicelluloses, cellulose, lignin, lipids and protein [2,3]. It is consequently feasible to achieve the resourceful usage of sewage sludge. Based on the existing sugar milling industry situation of the world, the bagasse, a residue of sugar milling, is needed to dispose. Bagasse is a major solid residue from sugar milling industry, and is also an ideal feedstock for renewable industry [4]. There were more than 70 million tons of sugarcane production annually, which produced about 7 million tons of sugarcane bagasse after sugar milling [5].

As a convenient route for the reduction of waste, incineration was broadly implemented worldwide. Approximately 55% of generated sewage sludge in Japan and 25% in Denmark were disposed by the incineration technology [6]. Although incineration had been proven as an efficient way for the resourceful usage of waste [7], the pretreatment and pollution control made a huge cost in the incineration [2]. Pyrolysis, the thermal destruction lacking of oxygen, could achieve huge reduction in waste volume, the stabilization of organic matter, as well as the production of fuels. Compared to incineration, pyrolysis converted the biomass energy into different types of bio-fuel, which provided a more flexible pattern for the usage of biomass energy. Hence, pyrolysis of solid waste attracted lots of attentions of researchers [8–11]. Alvarez et al. found that the catalytic activity of the sludge ash promoted the bio-oil formation [12]. Lin et al. had observed that the thermochemical reactivity was improved at low temperature on the co-pyrolysis of oil-palm solid wastes and paper sludge [13]. They attributed into the hydrogenation and thermal catalytic effects. Fang et al. had investigated the catalytic co-pyrolysis process with metal oxide, such as MgO, Al_2O_3 and ZnO [14]. With the addition of metal oxide, the pyrolysis reaction began at lower temperature, and the apparent activation energy was significantly reduced. In our previous work [11], we had studied the co-pyrolysis interaction between oil shale and sewage sludge using TG-FTIR system. Interestingly, low proportion of sludge blending with oil shale could improve the production of methane. The pyrolysis behavior of mixed materials was distinctly improved because of the presence of sludge. Nevertheless, the trial on bagasse pyrolysis with adding sludge was seldom reported.

The current researches on pyrolysis of bagasse focused on the improvement of bio-oil and bio-char [15–19], which provided useful information for the subsequent usage of pyrolysis products. However, the further investigation on reaction pathway was rarely performed, especially the co-pyrolysis reaction pathway. In this paper, KBr Pellets - by Infrared Spectroscopy, TG-FTIR and Py-GC/MS system were used in the co-pyrolysis process of bagasse and sewage sludge. The knowledge

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Table 1
The ultimate analyses and proximate analyses of bagasse and sludge on dry basis.

Samples	Ultimate analysis (wt.%)					Proximate analysis (wt.%)		
	C	H	O	N	S	Volatile	Fixed carbon	Ash
Bagasse	44.2	6.517	42.78	0.67	0.196	67.18	27.15	5.63
Sludge	22.21	4.013	17.51	3.42	0.464	33.38	13.97	52.39

obtained from these methods presented the basic information for co-pyrolysis process of bagasse and sewage sludge, which was significant for the development of co-utilization technique.

2. Materials and methods

2.1. Materials

The sewage sludge used in this study was obtained from Liede Wastewater Treatment Plant of Guangzhou, China. The bagasse was collected from Zhanjiang, Guangdong province of China. Samples were put in the loft drier, holding at 105 °C for 48 h air-drying. Then, dried samples were crushed and sieved. Finally, the particles less than 178 μm was obtained. The ultimate and proximate analysis results were shown in Table 1. The test of ash was performed on wavelength dispersive X-ray fluorescence Axio Pw4400 (Holland, PANalytical B.V.), and the results were presented in Table 2. Sludge was accounted for the weight proportion of 10%, 30% and 50% in the blends, which were named as 0.1sludge, 0.3sludge and 0.5sludge, respectively.

2.2. Experimental facility and methods

2.2.1. KBr-Tabletting based FTIR

Nicolet™iS™ 10 FT-IR spectrometer was used to obtain the KBr-Tabletting based spectrum of bagasse and sludge. FTIR analysis was used as a qualitative technique for analyzing the functional groups of materials. This method was based on the characteristic peak separations of FTIR spectra, which has been employed widely in previous researches [20,21]. The separation theory was that: the experimental spectrum $E_{exp}(x)$ was assumed a superposition of groups of single characteristic peaks $Z_i(x)$ $(i = 1, 2, \ldots, n)$, and matching functions were used to search for these peaks.

Table 2
The result of X-ray Fluorescence on ash (XRF) of sewage sludge on dry basis.

Ash composition (XRF)	wt.%
SiO_2	52.77
Al_2O_3	22.32
P_2O_5	9.65
Fe_2O_3	6.22
K_2O	3.21
CaO	2.77
MgO	1.19
TIO_2	0.7
SO_3	0.43
MnO	0.21
Na_2O	0.13
Cr_2O_3	0.09
ZnO	0.08
BaO	0.06
NiO	0.05
CuO	0.04
SrO	0.03
ZrO_2	0.02
Cl	0.02
As_2O_3	0.01

$$E_{\exp}(x) = \sum Z_i(x) \tag{1}$$

Each of characteristic peak was simulated by Gauss-Lorentz Amplitude function:

$$Z_i(x) = a_3 G_i(x) + (1-a_3) L_i(x) \tag{2}$$

Specifically, Gauss and Lorentz Amplitude were expressed as below:

$$G_i(x) = a_{0_i} \exp\left[-\frac{(x-a_{1_i})^2}{2a_{2_i}^2}\right] \tag{3}$$

$$L_i(x) = \frac{a_{0_i}}{1 + \left[\frac{(x-a_{1_i})}{a_{2_i}}\right]^2} \tag{4}$$

Software Peakfit 4.0 was used to separate the characteristic peaks of functional groups. The FTIR spectra was recorded from 4000 to 900 cm^{-1}.

2.2.2. TG-FTIR

To investigate the pyrolysis behavior of bagasse, sewage sludge and their blends, TG-FTIR experiments were carried out by using thermogravimetric analyzer (METTLER TOLEDO TGA/DSC1) coupled with Fourier transform infrared measurements (Nicolet™iS™ 10 FT-IR spectrometer). The temperature precision of TGA is ± 0.5 °C and sensitivity of microbalance is lower than ± 0.1 μg. Pure N_2 was used as the agent gas at a flowing rate of 80 ml/min. All of samples were kept at the weight of 10 ± 0.5 mg for reducing heat transfer limitation. It was heated from 50 °C to 1100 °C with the heating rate of 20 °C/min. In addition, the volatiles released during co-pyrolysis process were detected online by FTIR spectrometer, in which spectra was recorded from 4000 to 900 cm^{-1}. FTIR analysis was carried out using a resolution of 4 cm^{-1} and 8 scan per sampling, and it started when the sample temperature reached at 100 °C. The transfer line and detector were heated at a constant temperature of 225 °C for preventing condensation. To eliminate the background signal, blank experiments were carried out before loading samples.

$TG(t)$ was defined as Eq. (5):

$$TG(t) = \frac{m_t}{m_0} \times 100\% \tag{5}$$

where m_0 and m_t represented the initial mass and the mass at temperature t, °C.

And $DTG(t)$,%/min, was defined as Eq. (6):

$$DTG(t) = \frac{d[TG(t)]}{dT} \tag{6}$$

where T, min, represented the time, and there was a relationship, $t = 20$ T, according to the heating rate.

2.2.3. Py-GC/MS

Py-GC/MS experiments were designed for studying more details about the distribution of organic products from co-pyrolysis process. In this study, CDS Pyroprobe 5200 HP pyrolyser (Chemical Data systems) connected with a gas chromatography/mass spectrometry (7890B GC System/5977A MSD) was used to perform these experiments. All of samples were kept at 1 ± 0.1 mg. Pyrolysis was performed at 700 °C for 20 s using a heating rate of 20 °C/ms. The temperatures of oven and transfer line were both 300 °C. The GC system equipped with a HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm), and its interface temperature was held on 300 °C. The GC oven started at 50 °C and was kept for 2.25 min. After that, the heating program was performed with a heating rate of 10 °C/min, and it finished when the oven temperature reached 300 °C. The GC oven was held on 300 °C for 5 min, then the GC program came into the end. Pure helium was used as agent gas of GC/MS with a flowing rate of 1 ml/min and a 1:50 split ratio. Mass spectra detecting covered a range of 35–300 amu. The compounds were