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Short Communication

Enhancing the quality of bio-oil and selectivity of phenols compounds from pyrolysis of anaerobic digested rice straw

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HIGHLIGHTS

- Anaerobic digested substrate was high value-added utilized by pyrolysis.
- The thermal decomposition characteristics of ADRS changed significantly.
- The pyrolysis selectivity of ADRS for 4-Vinylphenol was improved.
- The yield of phenols increased after anaerobic digestion treatment.

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ABSTRACT

This study investigated the thermal decomposition characteristics and pyrolytic products of anaerobic digested rice straw (ADRS) by thermogravimetric (TG) and pyrolysis–gas chromatograph/mass spectrometry (Py-GC/MS) analysis. Compared with the raw rice straw (RS), the thermal decomposition temperature of ADRS was shifted to higher temperature zone and the second decomposition zone of cellulose ($T_{offset(c)} - T_{peak}$) became narrower (14 °C less), which indicated that the composition of rice straw were changed significantly by the anaerobic digestion pretreatment. Py-GC/MS analysis showed that the quality of the bio-oil and the selectivity of pyrolytic products could be obviously improved by anaerobic digestion. The total yields of alcohols, acids, aldehydes, furans, anhydrosugars, and ketones pyrolysis substances decreased, while the yield of phenols increased. The yield of 4-Vinylphenol (4-VP) increased from 29.33%, 8.21% and 5.76% to 34.93%, 12.46% and 7.68% at 330, 450 and 650 °C, respectively, after anaerobic digestion.

1. Introduction

Nowadays the environmental damages such as the acid rain, urban smog and global warming caused by emission from fossil fuels, have driven the world to search for new renewable alternative energy sources (Saidur et al., 2011). Biomass, as a less-harmful resource, is not only abundant around the world but also has enormous potential to be converted to various kinds of biofuels and biochemicals. As a bioresource, rice straw is one of the most abundant agricultural residues in Asian, and the production of such a resource can reach 650–975 million tons per year globally (Binod et al., 2010). Nowadays, most of them are left in the field and burned, which will cause severe environmental pollution problems and consequently affect the public health (Park et al., 2014). Therefore, it is meaningful for rice straw high valued and environmental utilization.

Anaerobic digestion technique has been successfully applied in biorefining and biomass conversion in several decades. However, the complex structure and composition of lignocellulose especially the slow lignin degradation in the hydrolysis phase lead to long digestion period and the low yield of methane production from anaerobic digestion (Mussoline et al., 2013). What's more, the low biodegraded anaerobic digested residue need to be further treatment. Recently some researchers in Europe utilized digestate from anaerobic digestion plant to produce pyrolysis oil, char and syngas suggesting that about 90% of the energy content of the biomass could be converted into usable products (Neumann et al., 2014). Therefore, according to the characteristics of rice straw anaerobic digestion treatment, we consider to utilize the lignocellulose classification combined anaerobic digestion with pyrolysis.

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Fast pyrolysis at moderate temperatures of around 500 °C and very short reaction times of up to 2 s has become of considerable thermo-chemical conversion technology. The process directly gives high yields of liquids of up to 75 wt.% which can be used in a variety of applications (Bridgwater, 2012). However, due to the high oxygen of biomass, the pyrolysis oil is complex, low energy density and chemically unstable. Thus, bio-oil still needs to be upgraded by lowering the oxygen content and removing residues further utilization (Bridgwater, 2012; Tsai et al., 2006). As mentioned above, during anaerobic digestion process, the degradation of sugars or soluble carbohydrate or enzymatic hydrolyzed sugars from hemicellulose, cellulose are easier to be utilized than lignin (Gunaseelan, 1997). Considering the alteration component and structure of lignocellulose, it may have a positive effect on utilization lignocellulose combined anaerobic digestion with pyrolysis. And the methods using anaerobic digestion as a method for lignocellulose pretreatment to improve the quality of bio-oil and the selectivity of pyrolytic products were rarely reported.

In this study, the thermal decomposition characteristics and pyrolytic products of rice straw anaerobic digestion was investigated. The effect of anaerobic digestion treatment on the pyrolysis products were examined by Py-GC/MS. Furthermore, the alterations of component and structure of anaerobic digested rice straw were also discussed in detail, to explore the relationship between anaerobic digestion treatment and thermal alteration of biomass pyrolysis, using components analysis, element analysis, Fourier translation infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and TG analysis.

2. Methods

2.1. Material

RS was collected from agricultural plots of South China Agricultural University in Guangdong, China. ADRS was separated and collected after more than 40 days treatment from the anaerobic digested residues which consist of rice straw, paper mill sludge and monosodium glutamate waste liquor. The samples were washed with distilled water and then naturally dried in air. The dried samples were crushed and stored for further use after passing through a screen of 60 mesh size.

2.2. Properties of materials analysis methods

Elemental analysis (C, H, N and S) of RS and ADRS was determined to use an elemental analyzer (Vario EL, Elementar, Germany). The cellulose, hemicellulose and lignin content of the samples were determined according to the modified Van Soest method (Liu, 2011). The ash content was measured by incineration of the dry samples in an electric muffle furnace at 575 °C for 4 h. In order to investigate the alterations of functional groups after anaerobic digestion treatment, RS and ADRS were measured by FT-IR spectra using the KBr pellet technique. Physical structure changes of ADRS were observed by SEM.

2.3. Thermal analysis with TGA

The thermal decomposition characteristics analysis of RS and ADRS were performed with a TGA instrument (TGA Q500) thermal analysis system. The measurements were carried out in 25 mL/min high purity nitrogen gas flow. Approximately 5 mg of sample was distributed in a platinum crucible and heated from room temperature to 110 °C in 4 min and kept for 30 min, then followed by a linear heating rate of 20 °C/min to 700 °C.

2.4. Py-GC/MS analysis

Py-GC/MS analysis was performed on a CDS 5200 series Pyrolyser connected to an Agilent GC 7890A/MSD 5975C. Samples were pyrolyzed at 330, 450 and 650 °C with the heating rate of 10 °C/ms for 10 s, respectively. The pyrolyser and GC/MS interface were kept at 280 and 300 °C, respectively. The volatile products qualitative analysis was conducted with HP-5MS 5% Phenyl Methyl Silox (30 m $\times$ 0.25 mm, i.e., film thickness 0.25 μm). The flow rate of He was 1.00 mL/min and a split ratio of 1:50. The GC oven was programmed from 50 °C (for 1 min) to 120 °C at a rate of 5 °C/min, then followed by 10 °C/min to 280 °C and held for 5 min. The mass spectrometer was operated in the EI mode using 70 eV of electron energy at a source temperature of 230 °C. The mass range of m/z 30–500 was scanned.

3. Result and discussion

3.1. Chemical characteristics analysis

3.1.1. Element and component analysis

The element contents and component of RS and ADRS were shown in Table 1. Compared with the RS, the C, H and O contents of ADRS decreased after more than 40 days treatment because the RS was degraded partly during anaerobic digestion process. The content of oxygen content decreased from 42.10% to 36.61%, which may increase the calorific value, decrease acids and improve the quality of bio-oil during the pyrolysis process (Liu et al., 2014). The increase of sulfur and nitrogen contents may be due to the long time soaking of materials in the digestion liquid, which contained monosodium glutamate waste liquor and paper mill sludge. However, no negative effect has been found on the pyrolytic products according to the Py-GC/MS experiment.

After anaerobic digestion treatment the relative content of cellulose and hemicellulose decreased from 35.65% and 34.42% to 25.82% and 30.70%, respectively. The relative content of lignin increased from 7.69% to 11.03% because it is more difficult to be degraded in anaerobic digestion process. It was supposed to be more conducive to produce phenolic compounds in pyrolysis. The increase of the relative content of ash was probably due to the mineralization of organic silicon. The composition alteration of biomass treated by anaerobic digestion might have a great influence on the thermal degradation behaviors and pyrolysis characteristics.

Table 1
Elemental and component analysis of samples.

Samples	Ultimate analysis (wt.% dry)					Component analysis (wt.% dry)				
	C	H	O[a]	N	S	Cellulose	Hemicellulose	Lignin	Ash	Others
RS	43.50 ± 0.45	6.33 ± 0.17	42.10 ± 0.17	0.59 ± 0.10	–	35.65 ± 0.30	34.42 ± 0.74	7.69 ± 0.11	7.49 ± 0.43	14.75 ± 0.83
ADRS	43.15 ± 0.04	6.16 ± 0.06	36.61 ± 0.05	1.31 ± 0.02	0.21 ± 0.10	25.82 ± 0.43	30.70 ± 0.86	11.03 ± 0.23	12.56 ± 0.15	19.89 ± 0.63

[a] Calculated by difference.