Studies on pyrolysis of wheat straw residues from ethanol production by solid-state fermentation

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Abstract

A new biomass, wheat straw residue (WSR) from ethanol production by solid-state fermentation was pyrolyzed in a fixed-bed at different temperatures 250–550 °C for 40 min with vacuum of 5 mmHg. The gas, oil and solid residue from pyrolysis process were investigated. GC analysis indicated that the pyrolyzed non-condensable gases mainly contained CO, CO₂, H₂, CH₄, C₂H₄ and C₂H₆. The HPLC analysis showed that glycolic acid (about 70% of water-soluble organic acids) in the oil was a major component.

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1. Introduction

Studies on degradation of lignocelluloses by chemical process have been given much attention because of the serious problem of limitations of fossil fuel reserves [1–3]. Among them, pyrolysis process is one of the selections, which has received increased interest for many years [4,5]. Pyrolysis processes have great potential for converting biomass into higher value fuels, chemicals and materials [6,7], which are carried out by heating the biomass in the absence of oxidizing agent around 500 °C [8–10]. The ingredients of pyrolysis products depend not only on pyrolysis reactor designing, the reaction parameters (such as temperature, residence time, pressure and heating rate), but also on the composition of the biomass used [11,12]. Including our work [13–15], studies on the thermochemical conversion of forest and agricultural residues have been previously done by many research groups [16–19]. Some studies on wheat straw pyrolysis have also been conducted [20–21,13]. However, pyrolysis of the wheat straw residue (WSR) from ethanol production by solid-state

fermentation has not been reported yet, so we are interested in this new material for pyrolysis studies and hope to find out some new results.

The aim of the present work is to study the WSR pyrolysis process, particularly the relationship between major products distribution and pyrolysis temperature. The chemical compositions of the pyrolysis oil were investigated by HPLC. The results obtained will be helpful for the further utilization of WSR and the improvement of pyrolysis process.

2. Materials and methods

2.1. Pyrolysis materials

The wheat straw residue (WSR) was supplied by Hongzhang Chen, our collaborator [22], in the Institute of Process Engineering, Chinese Academy of Sciences. The WSR was produced from the process of ethanol production by solid-state fermentation. The process begins with the treatment of steam-exploded wheat straw, follows simultaneous saccharification with a complex cellulase and fermentation using alcohol yeast. The complex cellulase includes exo- β -1,4-glucanase, endo- β -1,4-glucanase and β -1,4-glucosidase. The WSR appears to be brown powder and its main composition is given in Table 1. It was dried at 60 °C before analysis and pyrolysis.

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Table 1
The analyses of wheat straw fermentation residue

Components analysis (wt.%)		Elemental analysis (wt.%)	
Cellulose	25.9	Carbon	50.0
Hemicelluloses	21.2	Hydrogen	7.5
Lignin	26.3	Nitrogen	1.4
Ash	6.8	Oxygen ^a	41.1

^a By difference.

2.2. Pyrolysis reactor and conditions

The pyrolysis apparatus used has been previously described [13–15] and its schematic diagram is shown in Fig. 1. The experimental apparatus consists of four main parts: tubular furnace pyrolysis reactor, electrical heater, temperature controller, condenser and vacuum system. The tubular furnace pyrolysis reactor is made of stainless steel tube with a length of 540 mm and inner diameter of 55 mm. The electrical heater is inserted into the tubular furnace. The outer side of the tube furnace is insulated with the glass wool 60 mm thick, which in turn is covered externally by steel 2 mm thick. The temperature of the tube furnace is measured by a thermocouple inside the tube. Gases and vapors generated by the process are led to an ice-water condenser where products are collected. Non-condensable gases are further depleted in a filter. The pyrolysis conditions are given as below: temperature: 250, 300, 350, 400, 450, 500, 550 °C; vacuum pressure: 5 mmHg; time: 40 min.

2.3. Characterization

The pyrolysis oil and solid residue were weighed and the pyrolysis gas was calculated by difference. C, H and N contents of samples were determined by using an EA 14401 element analyzer. Oxygen content was calculated by difference based on an assumption that the samples mainly contained the elements of C, H, N and O. The higher heating value (HHV) of samples was calculated based on the Dulong formula [23]:

$$\text{HHV (MJ/kg)} = 0.3383 * C + 1.442 * (H - O/8) \quad (1)$$

In which, C, H and O represent the weight percentages of carbon, hydrogen and oxygen, respectively.

GC analysis with thermal conductivity detector (TCD) was performed using a Varian CP-3380 (for H₂, CO and CH₄) with Ar carrier gas and 5A molecular sieve column (3 m length, 80 °C), a CP-3800 (for CO₂, C₂H₄ and C₂H₆) gas chromatograph with He carrier gas and Propak-Q column (3 m length, 50 °C). The TCD temperature was 130 °C. The retention times (minutes) are H₂: 1.173, CH₄: 3.746, CO: 4.657 and CO₂: 2.654, C₂H₄: 2.911, C₂H₆: 3.103.

The analysis of pyrolysis oil was performed on HPLC system (GRE-3A Shimadzu) equipped with a Waters Model 401 refractive index detector and a Transgenomic ICsep ICE-ORH-801 column (300 mm × 6.5 mm). The mobile phase was 0.005 mol/l sulfuric acid at 0.6 ml/min, the injection volume was 10 µl and the column temperature was maintained at 48 °C. The HPLC peaks were labeled based on the identical retention time with the standard samples. The identification of glycolic acid was performed on HPLC/Q-ToF MS system (Micromass Q-ToF micro) with a UV detector and a Transgenomic ICsep ICE-ORH-801 column (300 mm × 6.5 mm). The mobile phase was super pure water at 0.6 ml/min, the injection volume was 10 µl and the column temperature was maintained at 48 °C. Q-ToF Micro ESI mass-spectrometer was operated in the positive ionization mode. The following settings were used. Capillary: 3500.0 V, sample cone: 20 V, extraction cone: 2.0 V, desolvation temperature: 250 °C, source temperature: 80 °C.

3. Results and discussion

3.1. Product distribution

Temperature has a significant effect on the distribution of pyrolysis products. As shown in Fig. 2, the oil yield increases from 0.7% at the beginning temperature of 250 °C to the maximum of 40.9% at 500 °C, and to 39.1% at the higher temperature of 550 °C in the experiment. At 250 °C, the residue of the feedstock is 95.2%. This value is considerably large because it is not charcoal but non-converted biomass (most probably un-reacted or slightly degraded) under this pyrolysis condition. The solid residue turns to charcoal at a relatively higher temperature. For instance, its value is 40.7% at 500 °C.

Fig. 1. Schematic diagram of the pyrolysis apparatus used: (1) furnace; (2) electrical heater; (3) stainless steel tubular furnace pyrolysis reactor; (4) thermocouple; (5) temperature controller; (6) and (7) condenser; (8) vacuum meter; (9) and (12) gas sampling valve; (10) and (11) sawdust cleaver; (13) vacuum pump.

Fig. 2. Effect of temperature on the yield of the different pyrolysis fractions.

For the gas fraction, its yield reaches to 22.4% at the highest pyrolysis temperature (550 °C) in the experiment. GC analysis shows that the pyrolyzed non-condensable gases mainly consist of CO, CO₂, H₂, CH₄, C₂H₄ and C₂H₆ with the quantity ratio of 42.2, 26.2, 12.7, 14.6, 3.4 and 0.9% at 500 °C, respectively.

3.2. Chemical analysis of pyrolysis residues

Solid residues were collected and analyzed by the elemental analyzer to determine the major elements such as carbon (C), hydrogen (H) and oxygen (O). The results of the elemental analysis are summarized in Table 2. It provides the evidence to support the pyrolysis mechanisms of two-reaction model [24,25]. The C/H atomic ratios measured in the solid residues ranged from an initial 0.56 in the dry sample to a maximum of 1.51 at 450 °C. The C/O atomic ratios of solid residues also increase gradually with pyrolysis temperature up to 400 °C. The products of this reaction stage below 400 °C mainly consist of intermediates and low molecular mass volatiles (e.g. H₂, CH₄, C₂H₄, C₂H₆, H₂O, etc). In the second stage mass change (400–550 °C), the intermediates further react to volatiles and solid residues. The mass percentage of C based on the initial sample decreased from 48.1 (at 300 °C) to 26.8 (at 550 °C) due to the pyrolysis reactions and the gasification of C to CO and CO₂ at the second stage mass change. The fact that final oil mass percentage is slightly smaller than that of oil at 500 °C shows that the effect of the second pyrolysis reactions of condensable gas has been remarkable at the pyrolysis temperature of 550 °C (Fig. 2). The higher heating values (HHV) of these solid residues were also measured, they all exceeded 20 MJ/kg.

Table 2
Effect of temperature on the C/H and C/O atomic ratios of pyrolysis residues

Temperature (°C)	60	250	300	350	400	450	500	550
C/H	0.56	0.72	1.01	1.22	1.33	1.51	1.49	1.55
C/O	1.62	1.71	1.97	2.28	2.46	3.38	3.41	3.46

Fig. 3. HPLC chromatograms of the water-soluble pyrolysis products.

3.3. Chemical analysis of pyrolysis oil

The pyrolysis oil at 500 °C was extracted with distilled water (1:10) and the oil was divided into water-soluble and water-insoluble fractions. The water-insoluble fraction of the oil was only about 7%. It means that the majority of the oil comes from the pyrolysis conversion of cellulose and semi-cellulose and only a little comes from the lignin at 500 °C.

Water phase was analyzed by HPLC. These peaks of the retention time consistent with standard samples were labeled in Fig. 3. However, it is necessary to point out that even if the peaks of the tested sample and the pure reagents have the identical retention time on a single column, it is not completely definitive to indicate that they are the same compounds. The further identification for the main peak was performed on HPLC/Q-ToF MS system. It shows that the water phase contains glycolic acid, which is about 70% of the total extract organic acids. And other acids, including acetic acid, hydroxybutanoic acid and formic acid comprise about 20–30%. The pH of the water phase is 2.3, which is mainly contributed by glycolic acid because it is not only large in quantity but also has high dissociation constant of $pK_a = 3.83$ (pK_a of formic acid = 3.75, pK_a of acetic acid = 4.76). Present results suggest that glycolic acid production is very important because it can be used for chemical feedstock. For example, biodegradable glycolic acid polymers are widely used for drug delivery systems.

Other low molecular pyrolysis products, such as oxalaldehyde, levoglucosan and hydroxyacetol are detected in the water phase. In comparison, absorbent cotton was also pyrolyzed. The result shows that the predominant product is levoglucosan in the pyrolysis oil. The above fact means that different materials would have different pyrolysis products. Ref. [26] has reported that main pyrolysis products of cellulose and xylan at 800 °C both also contain glycolic acid.

4. Conclusion

The residue of wheat straw fermented to yield ethanol was pyrolyzed at different pyrolysis temperatures from 250 to

550 °C with vacuum of 5 mmHg. The pyrolysis temperature had a significant effect on pyrolysis products distribution. At low pyrolysis temperatures (<450 °C), the solid residue was the main product. The pyrolysis oil and charcoal were almost equal at higher temperatures 500 and 550 °C. The maximum bio-oil yield of 40.7% was obtained at a pyrolysis temperature of 500 °C. GC analysis indicated that the pyrolyzed non-condensable gases mainly contained CO (42.2%), CO₂ (26.2%), H₂ (12.7%), CH₄ (14.6%), C₂H₄ (3.4%) and C₂H₆ (0.9%) at 500 °C. The analysis of the pyrolysis products by HPLC showed that there were plenty of organic acids in the pyrolysis oil, and glycolic acid was major one. The study is helpful to further obtain the value-added products using WSR.

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