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Quantitative comparison of different chemical pretreatment methods on chemical structure and pyrolysis characteristics of corncobs

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ABSTRACT

In order to identify the effects of different chemical pretreatment methods on structure changes of corncobs and their subsequent pyrolysis characteristics, the chemical pretreatment of corncobs was performed using different concentrations of sodium hydroxide (NaOH), sulfuric acid (H₂SO₄), and hydrogen peroxide (H₂O₂) solutions. The structure changes of corncobs were characterized by elemental analysis, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD). The pyrolysis characteristics of raw and pretreated corncobs were conducted on thermogravimetric analyzer (TGA) and pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS). TG/DTG analysis of raw and pretreated corncobs demonstrated that the rank order for the ease of pyrolysis was untreated < 1% NaOH < 1% H₂O₂ < 2% NaOH < 2% H₂SO₄ < 1% H₂SO₄. Py–GC/MS analysis showed that chemical pretreatment can effectively promote the production of furans and levoglucosan (LG) and inhibit the formation of acetic acid, ketones and phenols. The rank order of LG yields from untreated and pretreated corncobs was untreated < 1% NaOH < 2% NaOH < 1% H₂O₂ < 1% H₂SO₄ < 2% H₂SO₄. The maximum yield of LG (15.01%) was obtained by fast pyrolysis of corncobs pretreated using 2% H₂SO₄. It was 18.53 times the yield of LG from untreated corncobs. The results could be mainly attributed to the passivation of alkali metal and alkali earth metal and the removal of hemicellulose and lignin fractions during pretreatment.

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1. Introduction

As a result of the rising concern over the possible future shortage of fossil oil and the protection of environment, considerable researches have been boosted into the development and utilization of renewable lignocellulosic biomass resources [1]. Owing to its unique chemical composition, biomass has the potential to partly replace fossil fuel resources for the production of liquid fuels, chemicals and materials [2]. Pyrolysis is the first step in any thermochemical biomass conversion processes. It has been considered as one of most promising technology to convert biomass into liquid, gas and solid productions with low cost. The product distributions from pyrolysis of biomass are strongly dependent upon the pyrolysis conditions. Fast pyrolysis of biomass at moderate temperature (500 °C), high heating rate (>1000 K/s) and short vapor residence time (<2 s) is usually selected for maximizing the liquid yield [3].

The liquid production from fast pyrolysis of biomass, namely bio-oil, contains an extensive spectrum of organic compounds such as acids, alcohols, aldehydes, ketones, furans, esters, phenols, anhydrosugars, and large molecular oligomers [4–8]. Thus bio-oil has the potential to be used as feedstock for producing value-added chemicals and hydrocarbon fuels. However, because of the complex chemical composition of bio-oil and the fact that the concentration of each compound is very low, the recovery of specific chemicals is difficult and uneconomical

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at present. In direct fast pyrolysis, the main constituents (hemicellulose, cellulose and lignin) in heterogeneous biomass simultaneously undergo complex thermal decomposition, which contributes to the composition complexity of bio-oil and low selectivity of specific chemicals. Pretreatment is an effective method to alter the chemical structure of biomass, thus improve the quality of bio-oil in subsequent fast pyrolysis [9]. The pretreatment methods prior to fast pyrolysis include torrefaction, hydrothermal pretreatment and chemical pretreatment. Recently, fast pyrolysis aided by torrefaction has attracted a growing attention [10,11]. In view of the discrepancy in thermal stability of three biomass components, most of reactive hemicellulose can be decomposed by torrefaction pretreatment, and the solid residue with less hemicellulose content is subsequently fast pyrolyzed to obtain high quality bio-oil. By the combination of torrefaction and fast pyrolysis, the main constituents are stepwise converted into the staged liquid products that are less complex than bio-oil produced from direct fast pyrolysis [10–12]. Hydrothermal pretreatment known as wet torrefaction is also used as a pretreatment method for fast pyrolysis to obtain higher quality bio-oil. The effective fractionation of biomass is achieved and the chemical structure of biomass is modified by hydrothermal pretreatment, which contribute to the change in pyrolysis mechanism of cellulose in hydrothermally pretreated biomass. Owing to the removal of hemicellulose and the significantly enhanced selectivity of cellulose thermal conversion into levoglucosan, the upgraded bio-oil with high levoglucosan content is obtained from fast pyrolysis of hydrothermally pretreated biomass, and the chemical composition of bio-oil is significantly improved [13,14].

Up to date, numbers of papers about the effect of chemical pretreatment on the quality of bio-oil have been published [15]. However, quantitative comparison of different chemical pretreatment methods on the chemical structure of biomass and subsequent fast pyrolysis behaviors were not well understood. Corncocks with the productivities of 30 million tons per year is one of main crop residue resources in China [16]. Currently, a great number of corncocks are directly burnt in fields. This results in severe environmental pollution and waste of resources. Therefore, corncocks were selected as biomass material in the present study. The chemical pretreatments of samples were conducted using different concentrations of sodium hydroxide (NaOH), sulfuric acid (H₂SO₄), and hydrogen peroxide (H₂O₂) solutions. Subsequently, bio-oils were produced from fast pyrolysis of pretreated corncocks in a semi-batch pyroprobe reactor. This study focused on examining the effect of different chemical pretreatments on the structure and pyrolysis characteristics of corncocks.

2. Experimental methods

2.1. Material preparation

Corncocks used in this study was acquired from Baodi feed mill, Tianjin, China. Prior to chemical pretreatment experiment, the samples were ground and sieved to a particle size of 60–80 mesh, and then dried at 105 °C for 8 h. The results of elemental and proximate analysis of the samples were listed in Table 1.

2.2. Chemical pretreatment experiment

Chemical pretreatment of corncocks by 1 wt.% or 2 wt.% H₂SO₄ and NaOH solutions (Solid/liquid ratio = 1:10) was carried out at 100 °C. Pretreatment of corncocks by 1 wt.% H₂O₂ solution was conducted at 80 °C. The pretreated corncocks were subsequently filtered off, washed thoroughly with deionized water and dried at 105 °C for 15 h. The elemental analysis of corncocks was conducted in an elemental analyzer (Vario EL cube, Elementar, Germany) for determination of C, H, N and S. Ash content of samples was determined by NREL method. The oxygen content on dry basis was calculated from subtracting a hundred percentage with contents of ash, carbon, hydrogen, nitrogen and sulfur.

2.3. FTIR analysis

The chemical structure of corncocks was investigated using FTIR spectroscopy. About 1 mg of the sample was carefully mixed with 300 mg of dry KBr and pressed into a tablet. The infrared spectra were acquired by means of a FTIR spectrometer (Nicolet 6700, Thermo Scientific, U.S.A.) between 4000 and 400 cm⁻¹ with a resolution of 4 cm⁻¹ and 32 scans. The spectra have been normalized to the highest peak in the fingerprint region between 2000 and 400 cm⁻¹. Peak areas and height values for bands assigned to aromatic skeletal of lignin were divided by the values of carbohydrate reference peaks to provide relative changes in the chemical structure of corncocks in chemical pretreatment [17].

2.4. XRD analysis

The overall crystalline of corncocks was examined by a X-ray diffractometer (X'Pert Pro MPD, PANalytical B.V., Netherlands) using Cu K α radiation (λ = 0.15406 nm) at 40 kV and 40 mA. The samples were scanned at a scanning rate of 2°/min from 2 θ = 5° to 50° with a step of

Table 1
Elemental analysis of untreated and pretreated corncocks.

Items	Elemental analysis (wt.%) ^a							
	C	H	N	S	O	Ash	H/C	O/C
Untreated	43.75	6.38	0.33	0.06	43.69	5.80	0.15	1.00
1% NaOH	43.31	6.73	0.12	ND ^b	46.49	3.36	0.16	1.07
2% NaOH	44.12	6.55	0.16	ND	45.66	3.51	0.15	1.03
1% H ₂ SO ₄	46.07	6.50	0.24	ND	44.42	2.76	0.14	0.96
2% H ₂ SO ₄	45.85	6.44	0.25	ND	44.92	2.54	0.14	0.98
1% H ₂ O ₂	45.88	6.69	0.06	ND	45.52	1.85	0.15	0.99

^a Dry basis.

^b Not detected.

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