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Study on the preparation of wood vinegar from biomass residues by carbonization process

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HIGHLIGHTS

- Cotton stalk was used to produce wood vinegar by carbonization process.
- The highest yield of the refined wood vinegar reaches 25% at 350 °C.
- The main organic components in the wood vinegars are acids, phenols and ketones.
- The presence of potassium restrains the formation of ketones.

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ABSTRACT

In the paper, the production of wood vinegar from Chinese fir sawdust (FS), cotton stalk (CS) and bamboo sawdust (BS) by carbonization process was addressed. The wood vinegar yield was investigated and the organic compounds contained were determined by gas chromatography and mass spectrometry. It was found that the refined wood vinegar yield of FS increased firstly and then decreased with increasing carbonization temperature and the highest yield reached about 25% in 350–450 °C. The relative contents of acids and ketones from FS decreased and that of phenols increased with increasing temperature. The relative contents of acids and phenols in the wood vinegars produced from the samples were in the order of BS > CS > FS and that of ketones reversed. KCl solution treatment caused a decrease in the relative contents of the phenols and ketones, but an increase in that of the acids in FS wood vinegar.

1. Introduction

Wood vinegar (WV) or Pyroligneous acid (PA) is an acidic reddish-brown aqueous liquid. It is obtained by clarifying the liquid product of the carbonization process of woods or wood residues from wood processing industry, tree branches, bamboo, crop straw, fruit shell and other biomaterials (Wei et al., 2010). WV is often used as insect repellent, odor remover, wood preservative, soil or foliar fertilizer and plant growth promoter or inhibitor, animal feed additive, coagulant in NR sheets' preparation. Until now, lots of the products have been applied in a wide variety of markets (Wu et al., 2014; Shiny and Remadevi, 2014; Mu et al., 2004; Ferreira et al., 2005; Baimark and Niamsa, 2009).

The properties and utilizations of wood vinegar have been widely researched and the utilization is closely related to its compositions. It is reported that the high concentration of the organic acids in the WV exhibited the high antimicrobial activity (Ma et al., 2011) and the phenolic compounds showed significant antioxidant activity, and demonstrated dosage dependency (Loo et al., 2007, 2008). Wood vinegar contains lots of very complicated organic components and over 200 compounds have been found in the wood vinegar obtained from different resources (Guillén et al., 2001). In China, there have been some researches only on the organic components contained in the wood vinegars obtained directly from the charcoal kiln or WV Company. The wood vinegars are produced from Mongolian oak, birch, apple tree and pear by carbonization process.

Based on the heating rate, pyrolysis process can be divided into three modes: fast, intermediate and slow. As a kind of pyrolysis technology with low heating rate, carbonization process has been widely used in the conversion process of agricultural and forestry residues into high added-value products (Xiong et al., 2014). During the carbonization process, the raw material is heated up in oxygen-free environment and volatile matters emits from the parent materials and the three-phase matters of charcoal, liquid

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products, and fuel gas are produced. As a high application value product, WV can be obtained by clarifying from the liquid products. During the process, the final carbonization temperature employed plays a notable role in the distribution of the three-phase products (Kwapinski et al., 2010; Angın, 2013).

The production and characterization of wood vinegar from rubberwood was studied by Ratanapisit et al. (2009) and it was found that the optimum condition of pyrolysis was obtained at the heating rate of 1.4 °C/min to the final temperature of 550 °C with a WV yield of 27.45%. The main ingredient contained in the WV was acetic acid and included the high content of methanol compared to the WV produced from other woods. Moreover, Şensöz (2003) also found that there was an obvious difference in the ingredients of the wood vinegar produced from different raw materials and under different process conditions. However, there have been very few papers reported about WV preparation and the influence of preparing condition and feedstock on the yields and compositions of the resultant wood vinegar.

In the paper, as agricultural and forestry residues, Chinese fir sawdust, cotton stalk and bamboo sawdust were chosen as the raw materials for the wood vinegar production. Because that the wood residue including the fir sawdust is the main biomaterials for the production of the wood vinegar (Wei et al., 2010), Chinese fir sawdust was chosen as main research object. The experiment was conducted on a vertical tubular carbonization reactor and the organic constituents of the resultant wood vinegar were analyzed and determined. Thus, the effect of carbonization temperature and feedstock type on the yields and organic constituents of the resultant wood vinegar could be investigated in detail. Furthermore, Chinese fir sawdust was pretreated by KCl solution and the resultant sample was carbonized in order to investigate the effect of the presence of potassium on the compositions of the resultant wood vinegar. The aim of the research was to provide a theoretical basis for the further development and utilization of WV.

2. Methods

2.1. Materials

Three agricultural and forestry residue samples, Chinese fir sawdust (FS), cotton stalk (CS) and bamboo sawdust (BS) were chosen as the raw materials for the investigation. Their proximate and ultimate analyses are shown in Table 1 and their ash analyses are listed in Table 2. The ash constituents of FS could not be determined due to its very low ash yield as shown in Table 1. Thus, the influence of the mineral matters contained in the biomass is slight and could be neglected. The samples were dried at 105 °C for 2 h in a thermostatic air-blower-driven drying oven (DXG-9073B-1, Fuma Laboratory Instrument Co., Shanghai, Temperature precision 1 °C). Then, the dried materials with the particle size of 0.5–3 mm were prepared using a grinding machine (FW-400A, Zhongxing Weiye Instrument Co., Beijing).

FS sample was immersed in KCl solution with a concentration of 20% in the ratio of 20 ml/g biomass for 12 h, then filtered and dried in an oven at 60 °C for 24 h. The dried samples were placed in the dry airtight container for the subsequent carbonization experiment. The charcoal powder (⩽0.5 mm) was prepared by Xiong et al. (2014) from FS carbonized under the final carbonization temperature of 550 °C.

2.2. Methods

2.2.1. Biomass carbonization

As illustrated in Fig. 1, the carbonization processes of the samples were carried out in a vertical quartz tube reactor with the body length of 970 mm and the internal diameter of 35 mm. There was a quartz frit used as a gas distributor in the center section of the tube reactor. The tube reactor was heated by an electric furnace (temperature precision 1 °C) based on the designed procedure. During every run, about 90 g sample was loaded on the quartz frit. A flow of dry nitrogen (99.999%, 200 ml/min) was purged into the tube reactor to provide an inert atmosphere. A gas chromatograph (GC2014, Japan SHIMADZU Company) was used to test the oxygen in the outlet gas. When there was no O_2 determined in the outlet gas, the reactor was heated from room temperature to the designed final temperature at 10 °C/min and held at the temperature for 30 min to ensure complete pyrolysis. The final carbonization temperature range was designed from 250 °C to 550 °C. At the end of each run, the reactor was cooled down in nitrogen atmosphere to room temperature and the liquid in the condenser was collected. The collected liquid product is considered as the crude wood vinegar in the research. The yield of the crude wood vinegar could be obtained by calculating the increase in weight of the condenser. Each experiment under the same temperature was repeated three times in order to obtain adequate liquid and ensure the yield accuracy. The product yield was the average value of the three trials.

2.2.2. Crude WV refining

According to the refining process shown in the literature (Wei et al, 2010), the crude wood vinegars prepared under the different carbonization temperature and from different raw materials were

Table 1
Proximate and ultimate analyses of the samples.

Samples	Proximate analysis (wt%, ad)				Ultimate analysis (wt%, ar)				
	M	*A*	*V*	*FC*	*C*	*H*	O	*N*	*S*
CS	4.25	3.78	72.11	19.86	46.19	3.09	38.82	0.84	0.39
BS	2.85	2.04	78.97	16.14	47.14	3.26	41.01	0.73	0.27
FS	2.13	1.64	80.67	15.56	50.60	2.62	36.69	0.91	0.03

M = moisture; *A* = ash; *V* = volatile yield; *FC* = fixed carbon yield; ad = air-dried basis; ar = as received basis.

Table 2
Ash analyses of the samples.

Samples	wt/%									
	SiO_2/%	Al_2O_3/%	Fe_2O_3/%	CaO/%	MgO/%	TiO_2/%	SO_3/%	K_2O/%	Na_2O/%	P_2O_5/%
CS	11.69	1.75	1.13	30.8	13.88	1.39	6.3	18.86	10.03	4.07
BS	37.04	1.51	2.99	11.67	3.15	1.8	6.15	27.6	3.67	4.39