



Effect of oxidation processing on the preparation of post-hydrothermolysis acid from cotton stalk

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ABSTRACT

The typical properties and yield of the refined hydrothermolitic acid (RHTA) and refined hydrothermolitic oxidation acid (RHOA) respectively prepared from cotton stalk by the hydrothermolysis process with and without hydrogen peroxide at 180–280 °C were investigated. The pH of RHOA at 180–260 °C is lower than that of RHTA. The yield of RHOA prepared at 180–280 °C is higher than that of RHTA except 230 °C. Besides, the variation trend of RHOA yield at 180–260 °C is in accordance with that of RHTA yield at 200–280 °C. The composition of RHTA and RHOA were determined using gas chromatography and mass spectrometry. The acids content of RHOA at 200 °C reaches the maximum. The phenols of RHOA at 200–230 °C is significantly higher than that of RHTA. Under oxidation atmosphere, the formation of ketones is inhibited and the secondary reactions of furan derivatives is promoted. Overall, the oxidation processing can alleviate the severe hydrothermolysis conditions for preparing post-hydrothermolysis acid.

1. Introduction

With the depletion of traditional fossil energy and the improvement of human-beings demand for development, exploiting alternative renewable sources for the production of fuels and value-added chemicals has already been in the extremely urgency. Biomass wastes, one of most clear and renewable resources, is abundant and easily available. Additionally, the high-effective utilization of biomass wastes is meaningful to avoid the environmental pollution caused by the conventional incineration of biomass wastes. Recently, there are many kinds of biomass wastes studied such as fir, cotton stalk, bamboo and walnut shell (Wei et al., 2010; Wu et al., 2015). Pyrolysis and hydrothermolysis are the main and promising thermochemical methods to convert biomass wastes into value-added products, such as bio-oils, bio-chars and bio-derived chemicals (Kumar et al., 2018; Xiong et al., 2014).

Wood vinegar, which is a high value-added aqueous by-products produced during the slow pyrolysis process of various biomass wastes, has attracted great attention throughout the world. Wei et al. had used a vertical pyrolytic retort loaded with walnut shell to prepare pyrolygneous acids at 90–450 °C and found the pyrolygneous acid showed a strong antimicrobial and inhibition activity (Wei et al., 2010). Ma et al. had reported that the enriched acids fraction and enriched phenols

fraction derived from the pyrolygneous acid exhibited high anti-microbial and antioxidant activity (Ma et al., 2011). Ma et al. had conducted the preparation and extraction of pyrolygneous acid and found that all extracts showed superior characters than synthetic antioxidants (Ma et al., 2013). Therefore, because of the excellent anti-microbial, inhibition and antioxidant activity, wood vinegar has been widely applied in food industry, medical industry, agriculture and forestry. Compared with the pyrolysis process, hydrothermolysis process can handle biomass feedstock with high moisture content. Particularly, in our previous work, the composition of the aqueous product from the hydrothermolysis process of biomass wastes was similar to that of the wood vinegar, even having more value-added chemicals (Wang et al., 2018). Thus, it is feasible to prepare such high-valued product, i.e., post-hydrothermolysis acid, via the hydrothermolysis process.

However, the hydrothermolysis process is conducted under high temperature and high pressure, resulting in the increases in energy consumption and process cost. Thus, it is necessary to not only alleviate the severity of hydrothermolysis conditions, but also improve the quality of post-hydrothermolysis acid as possible. Wet oxidation is a well-established technique with typical reaction conditions of elevated temperatures (100–320 °C) and pressures (0.5–20 MPa) using

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homogeneous or heterogeneous oxidizers (Jain et al., 2016). There are several works pointing out that glucose facilitated the formation of the enriched acids products during the wet oxidation process (Calvo and Vallejo, 2002; Imbierowicz et al., 2015). In addition, it is well known that saccharides is the primary decomposed product during the hydrothermolysis process of biomass. Therefore, the hydrothermolysis oxidation process is potential to prepare the post-hydrothermolysis acid with abundant acids, as supported by the results that the content of acetic acid prepared by the hydrothermolysis process of 180–260 °C with an oxidative process was higher than that without oxidative process (Yousefifar et al., 2017). As a result, the aim of this work is to investigate the effect of oxidation processing on the typical properties of the post-hydrothermolysis acid.

Cotton stalk, one of typical agricultural biomass wastes in China, was selected as raw material in this work. Hydrogen peroxide, which is low-priced and has no hazard effect to the environment as its degradation products is oxygen and water, was used as oxidizer. The post-hydrothermolysis acid was prepared by the hydrothermolysis process from cotton stalk at 180, 200, 230, 260 and 280 °C with or without hydrogen peroxide, respectively. The typical properties and the yield of the post-hydrothermolysis acid were measured. Besides, the characteristics of the post-hydrothermolysis acid was determined using the gas chromatography and mass spectrometry. In particular, this study will provide a fundamental guide for the preparation and utilization of the post-hydrothermolysis acid.

2. Materials and methods

2.1. Materials

Cotton stalk (CS), collected from a cotton textile mill (Xinjiang, China), was used as raw material. The barked CS was ground into particle and sieved using a 0.50 mm sieve, followed by drying at 105 °C for 24 h in an oven (DXG-9073B-1, Fuma Laboratory Instrument Co., Shanghai). The dried material was stored in a desiccator for the further use. Hydrogen peroxide and diethyl ether (analytical grade) were purchased from Lingfeng Chemical Reagent Co. (Shanghai, China).

2.2. Hydrothermolysis processing

Typically, 10 g of CS and 100 mL of deionized water was placed into a 1L autoclave reactor (FCF-1L, Tianheng Instrument Co., Shanghai) and then agitated for 10 min to ensure the well mixing. Thereafter, the reactor was purged with nitrogen at a rate of 50 mL/min to exhaust the inner air. After no oxygen was detected by a gas chromatograph (GC2014, SHIMADZU Instrument Co., Japan), the reactor was sealed and then heated from room temperature to 180, 200, 230, 260 and 280 °C with continuously stirring at 600 rpm. Once the final temperature reached, the reactor was immediately cooled down with a water-bath to stop the reaction.

Subsequently, the suspension was separated via a vacuum filtration procedure to obtain the liquid product and CS char. The obtained liquid product was designated as the crude hydrothermolysis acid (CHTA) and stored in an amber laboratory bottle for the next experiment.

2.3. Hydrothermolysis oxidation processing

In the typical experiment, 10 g of CS and 80 mL of deionized water were firstly loaded into the reactor and then agitated for 10 min. Subsequently, a nitrogen flow at a rate of 50 mL/min was purging into the reactor to remove the residual air. After no oxygen was detected, 20 mL of hydrogen peroxide was injected into the reactor prior to the seal. After that, similar to Section 2.2, the reactor was heated from room temperature to 180, 200, 230, 260 and 280 °C with continuously stirring at 600 rpm. Once the final temperature reached, the reactor was immediately cooled down with a water-bath to stop the reaction. After

a vacuum filtration procedure, the obtained liquid product was designated as the crude hydrothermolysis oxidation acid (CHOA) and stored in an amber laboratory bottle for the next experiment.

2.4. Refining processing

Due to the advantage of the combination method of nature precipitation and cooling separation mentioned in our previous work (Wang et al., 2018), CHTA or CHOA was stood for 15 days at 25 °C and then stored at 3 °C for 48 h in a constant temperature circumstance by regulating temperature. After that, there were three layers appeared: a thin layer of oil on the top, a thick layer of aqueous liquid in the middle, and a thin layer of viscous tar in the bottom. The aqueous liquid was effective and value-added product, and designated as the refined hydrothermolysis acid (RHTA) or hydrothermolysis oxidation acid (RHOA), correspondingly. Afterwards, RHTA or RHOA was siphoned out and transferred to an amber laboratory bottle for the further analysis. In consideration of the similarity between the wood vinegar and post-hydrothermolysis acid (RHTA and RHOA) and the commercial standards of the wood vinegar applied to agriculture in South Korea and Japan (Choi et al., 2012), the typical properties, i.e., density, baume gravity, refraction index and pH were measured using an acidometer (PHS-3C, Youke Instrument Co., Shanghai) and a densitometer (XF-120YT, Xiongfeng Instrument Co., Fujian). The typical properties of RHTA and RHOA are listed in Table 1. The yield of RHTA and RHOA were calculated by Eqs. (1) and (2), respectively.

$$\text{RHTA yield (wt. \%)} = \frac{W_{\text{RHTA}} + \Delta W_1}{W_{\text{CS}} + W_{\text{H}_2\text{O}}} \quad (1)$$

$$\text{RHOA yield (wt. \%)} = \frac{W_{\text{RHOA}} + \Delta W_2}{W_{\text{CS}} + W_{\text{H}_2\text{O}} + W_{\text{H}_2\text{O}_2}} \quad (2)$$

where, W_{RHTA} and W_{RHOA} are respectively the weight of RHTA and RHOA obtained by difference, ΔW_1 is the difference of the hydrothermolysis CS char weight before and after drying at 105 °C for 24 h, ΔW_2 is the hydrothermolysis oxidation CS char weight before and after drying at 105 °C for 24 h, W_{CS} and $W_{\text{H}_2\text{O}}$ are the weight of CS and deionized water, respectively.

2.5. Characterization

It is necessary to conduct an extraction procedure for RHTA or RHOA prior to analysis. 40 mL of RHTA or RHOA was subjected to the extraction with 5 mL ether for five times. The ether left in the resulted sample was removed by a water-bath heating at 40 °C. Then, the sample was dehydrated by anhydrous magnesium sulfate powder prior to gas chromatographic and mass spectrometry analysis.

The chemical compounds in RHTA or RHOA was determined using the gas chromatography and mass spectrometry (GC-MS, Agilent 19091S-433-HP-5MS, America) with a HP-INNOWAX (30 m × 0.25 mm × 0.25 μm). The GC-MS conditions was listed in our

Table 1
Typical properties of RHTA and RHOA.

Sample	Temperature (°C)	Density (g/cm ³)	Baume (Be)	Refraction index (Brix)	pH
RHTA	180	1.007	1.003	1.824	4.85
	200	1.007	1.003	1.824	4.07
	230	1.004	0.574	1.044	3.92
	260	1.007	1.004	1.824	4.00
	280	1.006	0.860	1.564	3.99
RHOA	180	1.012	1.711	3.111	3.19
	200	1.009	1.287	2.340	3.22
	230	1.010	1.428	2.596	3.47
	260	1.007	1.003	1.824	3.87
	280	1.007	1.003	1.824	4.07

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