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Study on an alternative approach for the preparation of wood vinegar from the hydrothermolysis process of cotton stalk

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ABSTRACT

The yield and pH of the refined aqueous product (RAP) prepared by the hydrothermolysis of cotton stalk (CS) were investigated using response surface methodology with the variation of three parameters: CS/water ratio of 0.05–0.15*w/w*, temperature of 180–280 °C, and retention time of 0–30 min. At the best formulation (0.05*w/w*, 264.36 °C and 0 min), the yield and pH of RAP were 82.8% and 3.95, respectively. Additionally, the organic compounds contained in RAP prepared under the respective optimal formulation (pH: 0.05*w/w*, 251.43 °C and 0 min, yield: 0.05*w/w*, 280.00 °C and 0 min) were determined by gas chromatography and mass spectrometry. The results show that the kinds of compounds in RAP are identical or similar to those in the wood vinegar (WV), but their contents is slightly higher than that of the WV. In sum, it is feasible that RAP has the enormous potential to be utilized as WV probably because of its higher quality and value than WV.

1. Introduction

Sustainable and friendly development has been fully implemented in the globe, resulting in that the fuels, chemicals and other useful products prepared from renewable resources will gradually replace fossil fuels in the next decade. Herbaceous biomass has been known as one of most promising sources of renewable energy for its low cost, low pollution gas emissions and readily collection. Among all typical herbaceous biomass, cotton stalk, as an immense potential alternative raw material for the production of wood vinegar, has drawn a great number of attentions in the world (Wu et al., 2015). In recent years, the thermochemical conversion of biomass has been widely investigated for the final value-add chemicals, biofuels, and food additives (Hashmi et al., 2017). However, there are many methods employed to diverse researches, including dry torrefaction, hydrothermolysis, microwave carbonization, etc. (Nair and Vinu, 2016; Wu et al., 2015). Therein, hydrothermolysis technology is being extensively applied to the degradation of hemicellulose, cellulose, and lignin monomer polymers, as well as the different species of biomass nowadays, because water is a clean and friendly substrate.

Hydrothermal processing is usually conducted in a stainless steel reactor in an inert atmosphere beyond 160 °C under high pressure, which is also divided into the three zones of sub-critical, critical and sup-critical according to the different range of operating pressure. Wei et al. had found that the hemicellulose extract could be effectively converted into acid compounds approximately at pH of 2 by exploring the 0.4% H_2SO_4 and the ethanol yield increased significantly via hydrothermolysis process (Wei et al., 2011). Similarly, Moniz et al. found the existence of acetic acid, hydroxymethylfufural, furfurals and phenolics during the hydrothermal processing of corn straw (Moniz et al., 2013). Meanwhile, Yousefifar et al. performed an oxidative and non-oxidative hydrothermal processing of cellulose at temperature range of 180–260 °C and found acetic acid could be produced as main potentially valuable by-products for its stableness and low oxidizability (Yousefifar et al., 2017). These results are in consistent with Gao et al., who concluded that small molecular compounds, such as phenols, ketones, sugars, carboxylic acids, etc., were contained in the aqueous phase (Gao et al., 2012). It is well known that lignin is mainly composed of three monomers (i.e., guaiacyl, syringyl and hydroxyphenyl group) and Arturi et al. studied the hydrothermal conversion of Kraft lignin and found that methoxybenzenes, guaiacols, catechols, alkylphenols and anisolic/phenolic dimers existed in the aqueous and oil phase, respectively (Arturi et al., 2017). Above all, the diverse value-added and useful chemicals could be acquired through the hydrothermal processing of three main components of biomass.

Additionally, it is worth noting that these chemical compounds are

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greatly similar to those in wood vinegar in terms of acids, phenols, ketones, furans, etc. (Wu et al., 2015). Besides, there are rarely researches conducted to determine whether aqueous fraction is feasible to be utilized as wood vinegar. Moreover, during the hydrothermal pretreatment of the residual biomass for charcoal preparation in our laboratory (Wu et al., 2018), it has been found that the liquid product shows a light yellow to bark brown color and has a smoky flavor, presenting some parallel characteristics in agreement with the wood vinegar. Consequently, the aim of this work is to investigate the yield and characteristics of the aqueous fraction by-product for finding the optimization condition and alternative approach to produce wood vinegar.

Response surface methodology (RSM) is a combination of mathematical and statistical methods to reveal the effect of the main parameters and interaction of two or more parameters (Zhong et al., 2012), which is contributed to the modeling and analyzing engineering problems (Karacan et al., 2007). Herein, Box-Behnken design (BBD) is a rotatable or nearly rotatable second-order multivariate technique based on three-level incomplete factorial design, and generally used to establish a response surface molding with experimental data. Compared with other standard design method such as Central Composite design, BBD has less times of total run and avoids the run at maximum value concurrently. Thus, the method is more economical and can protect and prolong the life of equipment.

As an agricultural residue, cotton stalk are potentially low-cost biomass source and abundant in China. Thus, in this study, cotton stalk was chosen as the feedstock for the aqueous product preparation through the hydrothermolysis process. The hydrothermolysis process was carried out, after which the yield and physicochemical properties of the aqueous product were determined and the interactive effects of three parameters including solid/liquid ratio of 0.05–0.15 *w/w*, hydrothermal temperature of 180–280 °C and retention time of 0–30 min, on the aqueous product were investigated by BBD and quadratic programming. Furthermore, the characteristics of the aqueous product were determined and the feasibility of its utilization as wood vinegar was evaluated. This study will provide a valuable guide for the development of the high quality wood vinegar production and the optimization of the preparation process.

2. Materials and methods

2.1. Materials

Cotton stalk (CS) was collected from a textile mill (Xinjiang, China). The air-dried and barked CS were firstly ground into 1 mm and then milled through a 35–100 mesh screen, followed by washing with deionized water and then drying in an oven (DXG-9073B-1, Fuma Laboratory Instrument Co., Shanghai) at 105 °C for 24 h. The torrefied materials were stored in sample glass bottles for further using. Additionally, the ether with analytical grade from Lingfeng Chemical Reagent Co. (Shanghai, China) was used in this study.

2.2. Experimental design

Box-Behnken design (BBD) is an incomplete three level factorial design, created on rotatable or nearly rotatable second-order designs. Meanwhile, it provides an efficient tool to study the effect of the three factors on the production of the aqueous product using the Design-Expert Software (Version 8.0.6. Stat-Ease, Inc., USA). Additionally, it avoids the experiments performed under extreme conditions and does not involve combinations for which all factors are simultaneously at their highest or lowest points. In the current study, there are an amount of fifteen experimental points formulated [$= 2n\ (n-1) + C_0$, where n is the number of investigated factors (3) and C_0 is the replicated number of the central point (3)] (Zhao et al., 2017). The independent variables selected for this study included the CS/water ratio (X_1), the temperature (X_2) and the retention time (X_3), which were considered as the prominent factors influencing the proportion of solid, liquid and gas phase during the hydrothermolysis process (Nizamuddin et al., 2017). All independent variables were investigated at low (−1), medium (0) and high (+1) levels as shown in Table 1. Correspondingly, the two dependent variables, i.e., the yield of the refined aqueous product (Y_1) and pH of the refined aqueous product (Y_2), were considered as the main measurement indexes in this study. For better finding the true functional relationships between the independent and dependent variables, non-liner quadratic response surface model with a consideration of parameters interactions was a suitable approximation for the calculation of predicted response.

Table 1
Experimental formulation and corresponding response value in Box-Behnken design.

Run	Independent variable			Dependent variable	
	X_1	X_2	X_3	Y_1	Y_2
1	0.15(1)	280(1)	15(0)	0.625	4.27
2	0.15(1)	230(0)	30(1)	0.542	4.09
3	0.10(0)	280(1)	30(1)	0.668	4.25
4	0.05(-1)	280(1)	15(0)	0.804	4.10
5	0.10(0)	280(1)	0(-1)	0.722	4.18
6	0.10(0)	230(0)	15(0)	0.659	4.04
7	0.10(0)	230(0)	15(0)	0.643	4.05
8	0.10(0)	230(0)	15(0)	0.654	4.05
9	0.05(-1)	230(0)	30(1)	0.747	4.02
10	0.10(0)	180(0)	30(1)	0.604	4.31
11	0.15(1)	230(0)	0(-1)	0.629	4.04
12	0.05(-1)	180(0)	15(0)	0.718	4.47
13	0.05(-1)	230(0)	0(-1)	0.806	3.93
14	0.10(0)	180(0)	0(-1)	0.659	4.52
15	0.15(1)	180(0)	15(0)	0.652	4.41

X_1: CS/water ratio (*w/w*), X_2: Temperature (°C), X_3: Retention time (min), Y_1: The yield of RAP, Y_2: The pH of RAP.

$$Y_i = \alpha_0 + \alpha_1 X_1 + \alpha_2 X_2 + \alpha_3 X_3 + \alpha_1\alpha_1 X_1^2 + \alpha_2\alpha_2 X_2^2 + \alpha_3\alpha_3 X_3^2 + \alpha_1\alpha_2 X_1 X_2 + \alpha_1\alpha_3 X_1 X_3 + \alpha_2\alpha_3 X_2 X_3$$

where, Y_i is the measured response, α_0 is intercept, α_1, α_2, α_3 are linear coefficients, $\alpha_1\alpha_1$, $\alpha_2\alpha_2$, $\alpha_3\alpha_3$ are quadratic coefficients and $\alpha_1\alpha_2$, $\alpha_1\alpha_3$, $\alpha_2\alpha_3$ are interactive coefficients.

2.3. Hydrothermolysis process

For the hydrothermolysis experiments, each formulation was conducted thrice to reduce the random error. According to the formulation shown in Table 1, 5–15 g CS was placed into a 1L autoclave reactor (FCF-1L, Tianheng Instrument Co., Shanghai) with 100 mL deionized water. Then, a continuous stirring procedure was performed for 5 min to ensure the well mixing. Thereafter, the reactor was sealed after a nitrogen flow (50 mL/min) was purging into the reactor to exhaust the inner air. The reactor was heated to the set temperature (180–280 °C) and remained for certain time (0–30 min). After that, the reactor was cooled down to room temperature with a water-bath to stop the reaction immediately. The obtained slurry was separated into CS char and crude aqueous product (CAP) via a vacuum filtration. The CAP was stored in a sample bottle in a dark place for the following experiment.

2.4. Refining experiment

In this typical experiment, the combination of nature precipitation and cooling separation method were employed in refining experiment. The nature precipitation method was used universally in the refining process of wood vinegar for better protecting the effective compounds and better separation efficiency (Wei et al., 2010). However, there exists a drawback that the complete separation of CAP needs 30 or more