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Study of a new combined method for pre-extraction of essential oils and catalytic fast pyrolysis of pine sawdust

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ABSTRACT

A new combined method for the pre-extraction of essential oils (EOs) and the uniformly dispersion of alkaline earth metal oxide (AEMO) on pine sawdust (PS) was investigated. EOs were firstly extracted from PS after mixing with a certain amount of AEMO through steam distillation (SD), and then the pretreated PS was utilized in the process of fast pyrolysis to produce the upgraded bio-oil. A maximum extraction yield of EOs was 1.61 wt% from PS mixed with 5 wt% CaO within 300 min, compared with 1.21 wt% from the control (raw PS). The proportion of alcohols in EOs increased significantly when using PS mixed with AEMO. When PS was pretreated by the combined AEMO mixing and SD, the content of hydrocarbons in organic phase of the bio-oil increased significantly while that of acids and $C_nH_mO_x$ decreased. The analysis of physicochemical properties for the bio-oil further demonstrated that the quality of bio-oil was improved based on the new pretreatment method. Furthermore, the maximum bio-oil yield was obtained at pyrolysis temperature of 500 °C in almost all cases.

1. Introduction

Fast pyrolysis technology is considered as one of the most promising technologies for converting renewable biomass resources into high-energy density liquid fuel called bio-oil [1–5]. But there are some drawbacks for the application of bio-oil as fuel, including high water and oxygen content, high viscosity, chemical instability and poor ignition characteristics [6–8]. Alkaline earth metal oxide (AEMO), especially CaO and MgO, have been extensively studied as an effective catalyst utilized by a mechanically mixing method to improve the quality of bio-oil in the process of biomass fast pyrolysis due to its low cost and relatively high catalytic activity [9–12]. Zhang et al. [13] reported that hydrocarbons in bio-oil increased significantly and acids almost disappeared while using 5 wt% CaO mixed with sawdust. Lu et al. [14] found that the addition of CaO significantly reduced the levels of anhydrosugars, and eliminated the acids, while it increased the formation of hydrocarbons and several light compounds.

A kind of valuable chemical, essential oils (EOs), is widely used as fragrances in cosmetics, scenting agents in a variety of household products (e.g. soaps, room air-fresheners and insect repellents), and intermediates in the synthesis of perfume chemicals [15,16]. It is reported that around 2 wt% EOs are present in forest plants, such as pine, fir, etc. [17]. It is a waste of resources that forest plants with high value EOs are directly converted into the crude bio-oil in the process of fast pyrolysis without firstly extraction. Although the extraction process of EOs is costly, it could be neutralized by the value of itself. EOs can be extracted by conventional steam distillation (SD) [18], microwave or ultrasound assisted extraction [19], as well as the innovative supercritical fluid extraction [20]. Among these, SD extraction at 100 °C is extensively utilized in industry due to only using a simply equipment and obtaining EOs with high yield and quality.

Considering AEMO does not volatilize at 100 °C, a pre-mixing between AEMO and forest plants might not affect the quality of EOs in process of SD extraction. The AEMO is expected to disperse uniformly due to the structures of forest plants being broken under the action of steam [21]. The quality of bio-oil could thus be enhanced when the pretreated biomass was used as materials in fast pyrolysis process. Based on the above analysis, a combined method for the pre-extraction of EOs and the uniformly dispersion of AEMO catalyst on pine sawdust (PS) are studied in the present work. Specifically, the PS is firstly mixed with a certain amount of AEMO; then, EOs are extracted by ST at 100 °C, the powder of AEMO as catalysts are dispersed uniformly in the PS under the action of steam. The pretreated PS can be further utilized in the process of

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biomass fast pyrolysis to produce the upgraded bio-oil.

The objectives of this study were (1) to develop a combined method for the extraction of EOs and the uniformly dispersion of AEMO on PS, (2) to analyze the effect of different AEMO on the distillation of EOs, and (3) to determine the effect of different AEMO on the catalytic pyrolysis of the pretreated PS.

2. Materials and methodology

2.1. Materials

The PS used in this study as raw material is cultivated extensively in the central and northern region of China. Prior to use, the sample was sieved to the size range of 0.3–1.0 mm and then stored in a preservation box at 4 °C. Proximate and ultimate analyses for the PS are shown in Table 1. Two different commercially available AEMO, CaO and MgO, were bought from Sinopharm Chemical Reagent Co. (Shanghai, China).

2.2. SD treatment and pyrolysis experiment

SD was carried out in a laboratory scale extraction system as shown in Fig. 1, which mainly consists of a steam generator, a fixed bed extractor and an EOs condenser. Approximately 400 g of deionized water in a 500 mL flask was heated by a heating mantle to generate steam with a constant flow rate of 0.7 kg/min/m^2. The fixed bed extractor was heated and maintained at 100 °C with a heating tape. In each run, 50 g PS mixed with AEMO in different ratios was first placed in the extractor. With the increase of distillation temperature, the generated steam gradually entered into the extractor and carried EOs to flow into the condenser, in which most of steam and EOs were condensed and collected. In order to study the influence of distillation time on the extraction of EOs, the distillation time was set at 15, 30, 45, 60, 90, 120, 180 and 300 min, respectively. To obtain the chemical compositions of EOs at different distillation times, a new flask was substituted for the used one when the distillation time reached to the set time.

The fast pyrolysis of PS was carried out in a special tubular reactor which had a high-temperature segment (HTS) and a low-temperature segment (LTS). The HTS was heated by a furnace with a single set-point temperature controller for up to a maximum working temperature of 1200 °C, and the LTS was placed out of the furnace (Fig. 1). For each experiment, 10.0 g of raw PS or pretreated PS was first put into a porcelain boat, which was placed into the LTS. Anoxic atmosphere was achieved by blowing N_2 with a flow rate of 300 mL/min during the whole process. When the furnace reached to the desired temperature, the porcelain boat was quickly pushed into the HTS. The vapors generated in the pyrolysis process flowed out of the tubular reactor and passed through the condensation system, in which the condensable vapors were quenched to the liquid bio-oil. Each experiment was performed at least three times.

2.3. Characterization

2.3.1. Pine sawdust (PS)

Proximate analysis was conducted according to the ASAE and ASTM standard. Ultimate analysis was performed on an Elementar Vario EL III cube CHNS elemental determinator (Elementar INC, Germany). The heating value of PS and the products was measured on a NASREN MTZW-A4 Calorific Analyzer (Shanghai, China). The content of AEMO in the raw PS and treated one were determined by an ICP-AES (NCS Testing Technology, China). About 100 mg sample (either the raw PS or treated one) was ashed in a muffle furnace and then digested in a Telfon vial using a mixture of concentrated acids ($HF:HNO_3 = 1:1$) solution at 120 °C for 12 h. After the evaporation of the excessive acids, the residue remain was then dissolved in 2.5 mL of 37% HCl and heated to boiling for a few seconds. Subsequently, the sample was quantitatively transferred in to a Telfon flask, and deionized water was added until the volume of the solution reached 50 mL. All the concentrations were assessed through a spreadsheet-based program.

2.3.2. Essential oils (EOs)

The chemical compositions of EOs were determined by gas chromatography and mass spectrometry (GC-MS) of a Shimadzu (Tokyo, Japan) GC-2010plus coupled to a mass selective detector. The GC was equipped with an Rtx-5MS capillary column (30 mm × 0.25 mm i.d. × 0.25 μm film thickness) and an AOC auto injector. The GC-MS was performed using the following conditions: carrier gas, helium; flow rate, 2 ml/min; spilt ratio, 1:5; injection volume, 1 μL; injector temperature, 270 °C; temperature program, from 50 to 280 °C at 6.75 °C/min; ionization energy, 70 eV. The identification of individual components was confirmed by comparing their mass spectra fragmentation patterns with those stored in the mass database (Wiley & NIST). In a typical GC-MS analysis, a test sample was prepared by dropping acetone (Aladdin, 99.9%) into 500 μL of EOs up to 2 ml. A calcium ion densimeter (PCa-1/1-01, Leici, Shanghai, China) with a measurement range from 10^{-5} to 10^{-1} mol/L was carried out to determine whether AEMO was present in the essential oils collected.

2.3.3. Bio-oil

The liquid product of pyrolysis was centrifuged at 1200 rpm for 2 h to separate the aqueous phase from the bio-oil. Then, the chemical composition of the organic liquid phase was analyzed by GC-MS, and a test sample was prepared as section 2.3.2 described. The water content of the bio-oil was determined by Karl Fischer titration according to ASTM standard (D 1744) on a Mettler Toledo DM143-SC. The pH value was measured by a pH meter (Ohaus Starter 3C, American) according to ASTM standard (D 7544-12). Density was determined by weighting 1 mL of sample which was measured with a syringe of 5 mL. In this present work, the chemical composition analysis was conducted for organic phase of bio-oil, while the other physicochemical properties analysis was conducted for typical bio-oils.

Table 1
Proximate and ultimate analysis of feedstock.

Feed stock	Properties									
	Proximate analysis (wt%)				Elemental analysis (wt%)					LHV(MJ/kg)
	Moisture	Ash	Volatile matter	Fixed carbon	C	H	N	S	O[a]	
Pine sawdust	9.96 ± 0.05	0.81 ± 0.01	78.75 ± 0.6	10.48 ± 0.06	50.43 ± 0.15	6.15 ± 0.05	0.12 ± 0.01	<0.1	42.40 ± 0.18	18.87 ± 0.2

[a] By difference.