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Influence of acetone addition on the physicochemical properties of bio-oils

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ABSTRACT

In order to improve the physicochemical properties of bio-oil, acetone at different mass concentrations (3 wt.%, 6 wt.%, 9 wt.%, 12 wt.% and 15 wt.%, respectively) was added into the bio-oil. The physicochemical properties of blank (untreated bio-oil) and blended bio-oil were investigated every 7 days for a storage period of 35 days. The results indicate that acetone had a significant effect on improving the physicochemical properties of bio-oil. In addition, it is shown that with acetone concentration increased, the final pH values were increased by 1.71, 3.43, 4.00, 6.29 and 8.00%, respectively. The final water contents were decreased by 5.45, 8.09, 9.44, 12.13 and 12.01%, respectively. The final viscosities were decreased by 37.20, 57.78, 71.92, 79.79 and 84.67%, respectively. FTIR and GC–MS data indicate that acetone likely inhibited some ageing reactions of bio-oil and acetone itself joined the ageing reactions which bring some new substances. But there was no obvious evidence showing the relationship between the effects and mass concentration of acetone.

1. Introduction

Bio-oil is the liquid product of biomass fast pyrolysis which has the potential to replace fossil fuel [1]. It is a clean and renewable energy which is easy to be transported [2]. However, the pyrolysis process is not thermally balanced so its product bio-oil is unsteady. The viscosity and water content will increase with storage time and as a consequence, bio-oil will delaminate. Such disadvantages keep bio-oil from large-scale applications [3].

According to recent studies [4,5], the root cause of ageing is ageing related reactions, such as esterification, etherification and polymerization. These reactions will enlarge polar differences among the bio-oil components and cause the formation of larger molecules, ultimately resulting in phase separation and increases in viscosity. There are several methods of improving stability of bio-oil [6]. Considering the simplicity, the low cost of some solvents and their beneficial effects on the oil properties, adding solvents seems to be the most practical approach for bio-oil quality upgrading [7].

Diebold et al. [8] proposed an alternative method of adding several kinds of solvent into the pyrolysis oil. The result suggested that methanol modified bio-oil was still a single-phase liquid and still met the ASTM No. 4 diesel fuel specification for viscosity even after 96 h exposure to 90 °C. Scholze [9] diluted the bio-oil with 20 wt% methanol then distill it. The average molecular weight of the treated bio-oil was decreased. There was much less precipitate of the treated bio-oil than the crude bio-oil after exposure at 50 °C for more than 2 years. As a result, it is a good way to improve stability of bio-oil by adding solvents, but how solvents influence the compositions of bio-oil is not revealed or detailed.

As a common organic solvent, acetone was chosen as additive of bio-oil in this research because it has low viscosity and density and its dissolving capacity is excellent. The objectives of this research were to add acetone at different mass concentrations into bio-oil and to investigate its effect on the physicochemical properties of the bio-oil during storage. Compositional and structural changes of pyrolysis oils were investigated by FTIR and GC–MS.

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2. Materials and methods

2.1. Bio-oil

The initial bio-oil, used for the stability tests, was produced by the fast pyrolysis of sawdust (pinewood) in a continuously fed bubbling fluidized bed reactor designed by the Biomass Energy Engineering Research Centre, School of Agriculture and Biology, Shanghai Jiao Tong University, PR China [10].

The bio-oil collection system is comprised of multistage condensers and electrostatic trap. The pyrolysis temperature (reaction temperature) was 500 °C and the fluidizing gas was nitrogen with a fluidization gas flow rate of 60 L/min. Prior to commencing the pyrolysis processing, the sawdust was milled (30–80 mesh) and dried for 24 h at 105 °C. To improve the productivity of the bio-oil, the pyrolysis vapour is condensed rapidly in the quaternary condenser. Cooling water from the circulating cold water machine is circulated in the multistage condensers to cool the hot pyrolysis vapour. Commonly, most water vapour is condensed in the first condenser and the heavy and light ends of the bio-oil can be separated primarily in the other condensers during the condensation.

Elemental analysis of carbon, hydrogen and nitrogen was performed using the Vario EL element analyser. The results obtained from the elemental analysis of sawdust (air dry basis) are shown in Table 1. The initial oil was found to have a lower heating value of 15.96 MJ kg^{-1}. Its density was 1.19 g ml^{-1} and its ash content was 0.19%. The bio-oil appeared to be a dark brown and single-phase liquid with irritant smell.

2.2. Ageing test

Acetone (typically reagent-grade quality) was added into the bio-oil at different mass concentrations (3%, 6%, 9%, 12% and 15 wt.% respectively). The blended bio-oil was stored in small sealed glass vials with a volume of 50 mL at 25 °C for 35 days.

Indexes such as water content, viscosity (25 °C) and pH value (25 °C) were measured before storage and on the 7th, 14th, 21st, 28th and 35th day, respectively. FTIR and GC–MS are suitable techniques to investigate the compositional and structural changes that occur in bio-oil, and these techniques were used pre- (on day 0) and post-storage (on the 35th day).

2.3. Analysis

The water content of the bio-oil was measured by ASTM E203 method using the moisture tester from Metrohm, type KFT TITRINO plus 870.

The viscosity of the bio-oil was measured by ASTM D445 method using capillary viscometer, type SYD-265H, from Shanghai Changji Geological Instrument Limited Company.

The pH value of the bio-oil was measured by pH-potentiometer method using a particular electrode for ion-poor media from Shanghai Leici Instrument Plant, type PHS-3CT.

The heating value of the bio-oil was measured by ASTM D240 method using the bomb calorimeter (pure oxygen environment) from Shanghai Changji Geological Instrument Limited Company, type XRY-1B.

The density of the bio-oil was measured by ASTM D5002 method using density determination apparatus from Shanghai Shenkai Petroleum Instrument Limited Company, type SYP1026-II.

The ash content of the bio-oil was measured by ASTM D2270 method using Ash Determination Apparatus from Shanghai Shenkai Petroleum Instrument Limited Company, type SYP1005-I.

All of the measurements were repeated in triplicate and the experimental repetitive errors meet the requirements of corresponding method. The average values are reported.

Compositional and structural changes in the pyrolysis oils were investigated using the FTIR spectroscopy analyser using Fourier Transform Infrared-Raman spectrometer from Bruker, type EQUINOX 55. For each sample, spectral range was between 4000 cm^{-1} and 370 cm^{-1} with a 0.44 cm^{-1} resolution ratio.

The GC–MS analysis was conducted using the GC–MS analyser from Perkin Elmer. The measurements used a fused silica capillary column (0.25 μm × 0.25 mm i.d. × 30 m). The column temperature was kept isothermal for 10 min at 40 °C, and then increased to 250 °C at 3 °C/min. The temperature of vaporization was kept at 280 °C. Helium was used as a carrier gas at a constant flow of 1.2 mL/min. A split injection with a split ratio was 10:1 and the sample size used was 1.0 μL. For each sample scanning, the quality range was between 0 u and 1200 u. The compounds were identified by their retention time and by comparison to mass spectra of well known compounds.

3. Results and discussion

3.1. Effect of adding acetone on the pH value

Due to the reasons that water content was increased and more hydrogen ions were dissolved in the water, the pH value of the bio-oil became smaller with storage. Fig. 1 shows the pH value (25 °C) of the bio-oils stored for 35 days.

The effect of acetone additive was analyaed by the ANOVA two-way repeated-measures. The results show that both the storage time and the additive concentration had significant influences on the pH value. Interactions of the two factors also had significant influences.

Table 1
Results of elemental analysis of sawdust (air dry basis).

Feedstock	C (wt%)	H (wt%)	N (wt%)	O and others (wt%)
Pine	48.42	5.51	0.30	45.77