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Optimization of composite additives for improving stability of bio-oils

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ABSTRACT

Composite additives of ethanol, acetonitrile, and methyl acetate were added to bio-oils to assess the effects of these additives on stability of bio-oil using D-optimal experimental mixture design (DMD). A systematic analysis of the influence of different proportions of composite additives on bio-oil properties such as viscosity, water content and pH was carried out. The results showed that bio-oil had a lower viscosity, water content and higher pH when the additive formulation consisted of 6.58 wt% ethanol, 1 wt% acetonitrile and 2.42 wt% methyl acetate that was determined to be an optimal composite additive (OCA). Experimental trials were performed to validate the models. A fast aging test at 80 °C for 24 h confirmed that the composite additive was better than single additives to improve stability of bio-oils. The viscosity of bio-oil with OCA was 27.25 mm^2/s and was reduced by 33–47% compared to the bio-oil with a single additive; while reduced by 95% with no additives. GC–MS analysis showed that several compounds such as 4-hydroxy-Butanoic acid, p-Cresol, and Vanillin were virtually eliminated in bio-oil with addition of the composite additive. This research illustrated the beneficial effect of the composite additive for storage of bio-oils.

1. Introduction

Rapid development of the economy and rising population in China creates greater pressure on energy resources and the environment, which has increased interest in renewable and sustainable energy. Among all sources of renewable energy, biomass is one of the most promising energy forms. Fast pyrolysis of biomass has become popular. It is a high temperature process where the biomass is heated rapidly in the absence of oxygen, and where the vapors are condensed to bio-oil. There are three products in fast pyrolysis process of biomass; bio-oil, bio-char, and fuel gas, respectively [1,2]. Bio-oil is a free-flowing, dark brown liquid with a distinctive smoky odor. Bio-oil is a potential liquid fuel as a substitute for fossil fuels with properties of lower S and N content, higher energy density and better transportability than the original feedstock. Bio-oil has several shortcomings: high water content, high viscosity, high ash content, low heating value, instability and is highly corrosive, which limits industrial applications [3]. Many aspects of bio-oil have been investigated, including pyrolysis to produce bio-oils [4–6], optimization of upgrading technologies [7,8], bio-oil characterization [9,10], transportation [11], storage [12,13] and applications [14].

When bio-oil is used as transportation fuel or for a raw material, the bio-oil storage for a long period is frequently necessary. However, storage stability of pyrolysis-derived bio-oil is a big challenge for applications of bio-oil. There are numerous methods such as removal of ash in the feedstock, hydrogenation, catalytic cracking, catalytic pyrolysis, molecular distillation, steam reforming, supercritical fluids, esterification and emulsification which have been developed to improve stability of bio-oil in storage. These methods have several shortcomings such as high energy consumption and high cost and operation complexity. To improve properties of bio-oil, addition of organic solvents has been proposed. The fact that the addition of organic additives can enhance bio-oil stability and reduce viscosity has been demonstrated by previous researches using various organic solvents, including isopropanol [15], acetone [16], methanol [17], ethanol [18] and an acetone–methanol mixture [19]. However, to the best of our knowledge, it is a rare publication where a composite additive has been developed and used to improve the storage stability of pyrolysis-derived bio-oil. Shanghai JiaoTong University has done some studies on composite additives to bio-oil. Zhang [20] use one-factor

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multi-objective optimization of the Design-Expert software to get an optimal mixed additive of bio-oil consisting of methanol, acetone, and ethyl acetate. However, multi-factors, multi-objective optimization of composite additive of bio-oil is urgently needed. In this study, the D-optimal experimental mixture design was used to develop a new composite additive consisting of ethanol, acetonitrile and methyl acetate.

2. Objective

The objective of this research was to develop an optimal composite additive to improve the physicochemical properties through a series of optimization processes. The experiment can be divided into two parts. First, a series of optimization experiments were performed and the optimal formula of the composite additive was determined. Second, research focused on investigating the effect of the optimal composite additive on characteristics of pyrolysis-bio-oil by using experimental techniques.

3. Materials and methods

3.1. Bio-oil samples

The bio-oil used was produced from fast pyrolysis of rice straw at 500 °C in a fluidized bed reactor. The bio-oils were known not to contain any chemical additives. After production, bio-oils were sealed in glass bottles and temporarily stored in a freezer at 4 °C for subsequent analysis.

3.2. Bio-oil analysis

3.2.1. Water content

Water content of bio-oil was analyzed by Karl-Fischer titration technique according to ASTM E 203. The precision was 0.01%. The instrument used was KFT 870 from Swiss Manthon Instrument.

3.2.2. pH value

The pH value of the bio-oil sample was tested at room temperature using a PHS-3C pH meter, Shanghai Lei Ci Instrument Corporation. Prior to the test, the instrument was calibrated using the standard buffer solutions with the pH value of 4.00 and 6.86.

3.2.3. Density

According to ASTM D 4502, the density of the bio-oil was measured using a density meter (DMA 4100M) from Anton Paar Corporation. The precision was 0.0001 g/cm^3.

3.2.4. Viscosity

Kinematic viscosity of bio-oil sample was measured according to ASTM D445 using a petroleum product kinematic viscosity tester (Shanghai Changji Geological Instruments Co., Ltd. SYD-265C).

3.2.5. GC–MS analysis

Composition of bio-oil samples was characterized using GC–MS (AutoSystem XL GC/TurboMass MS, Perkin Elmer) with a quadruple detector and a DB-1MS capillary column (30 m × 0.25 mm inner diameter × 0.25 μm thickness). The carrier gas was helium (UHP) with a constant flow of 1.2 mL/min. The oven temperature program had an initial temperature of 40 °C held for 4.0 min, rising by 5 °C/min to 250 °C, which was held for 10.0 min. The injector temperature was 250 °C. A sample volume of 1 μL (10% of pyrolysis liquid in chloroform) was injected. Electron ionization (EI) was used in the MS and standard mass spectra with 70 eV ionization energy was recorded over a scanned range from 0 to 1200 amu. The computer matching of the mass spectra with the NIST98 and WILEY7.0 libraries and the retention times of known species injected in the chromatographic column were used for the identification of the peaks. Compounds considered for qualitative and semi-quantitative analysis were ones whose minimum similarity match was equal or higher than 700.

3.2.6. Microscopic analysis

The microscopic analysis of bio-oil samples was performed by lightly pressing a tiny drop of bio-oil sample between the glass slide and cover glass. Micrographs were taken using a built-in camera with a magnification of the microscope at 50×.

3.3. D-optimal experimental mixture design

D-optimal experimental mixture design is a special type of response surface experiment in which the factors are the components of a mixture and the response is a function of the proportions of each ingredient. This approach is suitable for blending problems with the least number of experiments. It involves changing mixture composition, exploring how such changes will affect the properties of the research object and choosing the optimal composition for achieving the prefixed target. Detail optimal formulation selection in given in Section 4.2. A comprehensive introduction of the D-optimal mixture design is given by Andersen-Cook et al. [21]and its application was studied by Abnisa et al. [22,23]. It is an effective way of optimizing complex processes.

In the present study, D-optimal mixture design by Design-Expert software (Stat-Ease Inc., Minneapolis, USA) was applied for development of the optimal composite additive mixture of bio-oil. The experimental mixture design is given in Table 1. With three components, ethanol, acetonitrile, and methyl acetate, the design consists of 16 experimental points. For the whole mixture experiments, sum of three components in the composite additive was always 10 wt%. Based on preliminary trials, each individual component in composite additive had the same lower constraint of 1 wt% and upper constraint of 8 wt%. According to configurations in Table 1, each composite additive candidate was prepared and added to the bio-oil sample. Variables such as viscosity, water content, pH, and density, were immediately tested after adding the composite additive. All experimental samples were sealed in bottles for accelerated aging. The aging experiments were carried out in incubator at 80 °C for 24 h [15]. The same variables were determined after the aging process. Viscosity index and water content index were calculated by Eqs. (1) and (2).

$$\text{Viscosity index } (40\,^{\circ}\text{C},\ \%) = (V_2 - V_1)/V_1 \times 100\% \quad (1)$$

$$\text{Water content index } (\%) = (W_2 - W_1)/W_1 \times 100\% \quad (2)$$

Table 1
The experimental mixture design.

Run	Components		
	Ethanol (wt%)	Acetonitrile (wt%)	Methyl acetate (wt%)
1	8.0	1.0	1.0
2	5.7	3.3	1.0
3	4.5	4.5	1.0
4	4.5	4.5	1.0
5	3.3	5.7	1.0
6	1.0	8.0	1.0
7	3.3	3.3	3.3
8	1.0	5.7	3.3
9	4.5	1.0	4.5
10	4.5	1.0	4.5
11	4.5	1.0	4.5
12	1.0	4.5	4.5
13	1.0	4.5	4.5
14	2.2	2.2	5.6
15	1.0	1.0	8.0
16	1.0	1.0	8.0