Fuel 211 (2018) 704–711

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Studying on properties of bio-oil by adding blended additive during aging

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ARTICLE INFO

Keywords:
Blended additive
Mixture design
Bio-oil aging
Storage properties

ABSTRACT

The effects of blended additive on properties of bio oil were investigated by adding *n*-butanol, dimethyl sulfoxide (DMSO) and ethyl acetate to bio-oil. The blended additive, which consisted of 2.421 wt% *n*-butanol, 2.327 wt% DMSO and 3.252 wt% ethyl acetate, was obtained through simplex lattice of mixture design. A 24 h aging experiment at 80 °C revealed that blended additive can improve bio-oil stability, and the effect of the blended additive was superior to that of a single additive. The viscosity of the bio-oil containing optimal blended additive was 8.21 mm^2/s, whereas that of a single additive ranged within 8.89–9.78 mm^2/s. During the long aging process (12, 24, 36 and 48 h), the increase in viscosity and water content of the blank group was larger than that of the control group. Thermo–gravimetric analysis (TGA) results showed that the residual mass fraction of the bio-oil rose with aging time, and the trend increase of blank was larger than that of control. Gas chromatography–mass spectrometer (GC–MS) findings showed that the content of phenols was highest in bio-oil samples and decreased with increasing aging duration. The total contents of ketones, aldehyde and furans diminished with aging time.

1. Introduction

With economic development, problems on energy shortage and environmental pollution greatly challenge sustainable global development. Biomass has attracted increasing attention as a kind of renewable energy [1]. Biomass is a clean energy containing small amounts of sulfur, nitrogen and ash; it emits lower levels of SO_2, NO_x, and soot than those released by conventional fossil fuels [2]. Biomass includes many types, such as crop, crop waste, wood, timber residues and animal wastes etc [3]. However, biomass holds some limitations. For instance, biomass contains substantial moisture that cannot support stable combustion and produces smoke in the combustion process. Moreover, biomass density is lower than fossil fuel density, and hence, augments transport costs. These problems hinder the direct use of this energy source.

The fast pyrolysis is a promising technology for biomass utilization [4]. Biomass fast pyrolysis can be achieved at around 500 °C in the absence of oxygen [5]. The fast pyrolysis process is convenient, and main products are combustible gas, bio-oil and solid biomass carbon [6]. Straw was used as material for fast pyrolysis to obtain bio-oil at 50%–55% and 15–16 MJ/kg heat values, as well as biochar at 28%–33% yield and 18–20 MJ/kg heat values [4]. Bio-oil exhibits a high energy density, and involves convenient transportation, storage and utilization. Biomass materials are also cheap and easy to acquire, and generates bio-oil under the fast pyrolysis of large biomass. Thus, the use of bio-oil as an alternative to fossil fuels has received increasing interest in recent years [7].

Although, bio-oil is widely regarded as an alternative to renewable energy sources, it possesses undesirable properties, such as high viscosity, water content and lower heat value, which impedes bio-oil's direct application as an actual fuel [8]. Bio-oil is composed of a mixture of many oxygen-containing compounds, such as acids, ketones, aldehydes and phenols etc. However, this feature provides both prospect and problem for bio-oil utilization. Some chemical feedstock can be extracted from bio-oil [9]. Under prolonged storage, bio-oil undergoes condensation, esterification and polymerization reactions because of oxygen-containing compounds [10]. These reactions increase the bio-oil viscosity and cause the formation of higher molecular species that eventually forms sludge at the bottom of the container. Nevertheless, bio-oil remains as a promising energy substitute. Many researchers study bio-oil, including the pyrolysis technology [11], upgrading [12], storage [13], transportation [14] and application [15] etc.

The storage stability of fuel is a crucial factor for industrial applications [16]. However, bio-oil is unstable, and its physical and chemical characteristics change during storage. The main methods for upgrading bio-oil quality are feedstock pretreatment [17], hydrodeoxygenation [18], esterification [19], emulsification [20], catalytic cracking [21], steam reforming [22], highly valuable chemicals extractions [23] and solvent addition [24] etc. Compared with other methods, solvent addition is more effective and convenient for upgrading bio-oil. Polar

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http://dx.doi.org/10.1016/j.fuel.2017.09.106
Received 11 August 2017; Received in revised form 25 September 2017; Accepted 27 September 2017

solvent has been demonstrated to reduce viscosity and enhance bio-oil stability [25]. Alpaslan Atmanli et al. demonstrated that *n*-butanol is a promising alternative fuel for stabilizing vegetable oil blend [26]. The response surface methodology was applied to study a mixture of diesel, n-butanol and vegetable oil, and the optimum mixing ratio is obtained according to engine operating parameters [27]. Many articles have also explored methanol, ethanol, acetone and ethyl acetate [28] etc. Solvent addition affects bio-oil storage primarily through three mechanisms:(1) physical dilution; (2) reduction of reactants concentration or reaction rate by changing the bio-oil microstructure; and (3) solvent reaction with the active component of bio-oil and prevention of macromolecular polymer generation [29]. Most studies directly add a single solvent to bio-oil. However, using blended solvent to upgrade bio-oil is insufficient. By contrast, blended additive helps enhance bio-oil storage time and prevents the viscosity increase [30].

Therefore, this study acquired a blended additive of n-butanol, DMSO and ethyl acetate by simplex lattice of mixture design. The response variables were viscosity, water content and pH. Samples were placed in an 80 °C incubator for 12, 24, 36 and 48 h. At each aging period, samples were analyzed using several analytical instruments including TGA, and GC–MS. According to the analysis results, the effects of blended additive on properties of bio-oil were investigated.

2. Materials and methods

2.1. Bio-oil and solvent

The bio-oil acquired by walnut shell fast pyrolysis in a nitrogen atmosphere was in the range 500 °C–550 °C. *n*-Butanol (≥99.5%, AR), DMSO (≥99.5%, AR) and ethyl acetate (≥99.5%, AR).

2.2. Bio-oil analysis

2.2.1. Physical properties

Viscosity is a physical property that is valuable to bio-oil utilization. The kinematic viscosity of bio-oil was measured by a SYD-265H petroleum product kinematic viscosity tester at 40 °C. The water content of bio-oil was measured using a Karl-Fischer titration apparatus ZDJ-35. The titration solvent is consisted of methanol and dichloromethane at a ratio of 1:3. The pH was measured through a pHB-8 pH meter at room temperature. Density was measured through a SYD-1884 petroleum product density meter at 25 °C. All samples were homogeneously mixed before testing.

2.2.2. GC–MS analysis

Bio-oil samples were further analyzed by GC–MS (Thermo Trace GC Ultra with an ISQ i mass spectrometer) equipped with a SE-30MS capillary column (50 m × 0.25 mm i.d × 0.25 μm film thickness) and a quadrupole analyzer in electron impact mode at 70 eV. Split injection was performed at a split ratio of 50 by using helium (99.999%) as carrier gas. The GC heating ramp was as followed: (1) maintained at 40 °C for 5 min, (2) heated to 180 °C at 5 °C /min and held at this temperature for 2 min, and (3) heated to 280 °C at 10 °C/min, and then maintained at this temperature for 5 min. The temperatures of interface, ion source and MS transfer line were all set to 280 °C. The compounds in the liquid product were identified through the NIST library, Wiley library and literature data. The injector temperature was 250 °C. A sample volume of 0.2 μl was injected.

2.2.3. TGA

The bio-oil samples were analyzed by using the TGAQ500 analyzer. Bio-oil samples were heated from 30 °C to 800 °C at a heating rate of 30 °C/min. The N_2 flow was 100 ml/min.

Table 1
Design of experimental scheme.

Run	Components		
	n-Butanol (wt%)	DMSO (wt%)	Ethyl acetate (wt%)
1	1.000	6.000	1.000
2	1.000	1.000	6.000
3	4.333	1.833	1.833
4	2.667	2.667	2.667
5	1.833	1.833	4.333
6	1.000	2.667	4.333
7	2.667	4.333	1.000
8	4.333	1.000	2.667
9	1.000	1.000	6.000
10	2.667	1.000	4.333
11	4.333	2.667	1.000
12	6.000	1.000	1.000
13	4.333	2.667	1.000
14	1.000	6.000	1.000
15	6.000	1.000	1.000
16	1.833	4.333	1.833
17	1.000	4.333	2.667

2.3. Design experiment

The design experiment aimed to acquire the optimal blended additive and studied the effects of the additives on bio-oil storage. Design-Expert is a professional software for experimental design and correlation analysis. The whole process consisted of three modules, namely, design, analysis and optimization. The process involves the change of components, the relationship between the components and response variables, and the selection of the optimal component. The simplex lattice of mixture design in Design-Expert creates the design by imposing a grid over the design space. The design is then augmented with interior points and point replicates to improve the estimating capabilities [31]. The massive benefit of a design experiment is the reduction of experimental trials and the effective handing of the blending problem.

The experiment was carried out through simplex lattice of mixture design. The experimental scheme design is shown in Table 1. Experiment adopted third order that involves four experiment levels to give a total of 17 experiments. The whole experimental optimization process is depicted in Fig. 1. The experimental components included *n*-butanol, DMSO and ethyl acetate. The total solvent content was 8 wt%, whereas that of the bio-oil was 92 wt%. Each component scaling value ranged from 1 wt% to 6 wt%. The experiments were carried out at 80 °C incubator for 24 h. The result was tested at the beginning and end of the experiment. All samples were homogeneously mixed before testing. Each experiment was tested three times and the averaged was obtained as results. The indexes of response variables are defined in Eqs. (1) and (2), respectively.

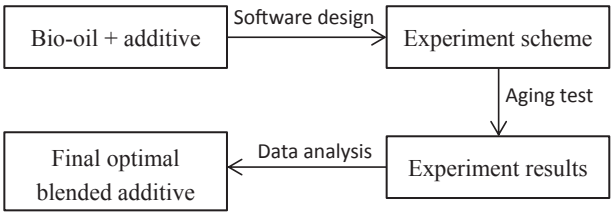

Fig. 1. Experimental optimization process.