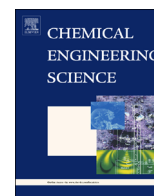




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Stability evaluation of fast pyrolysis oil from rice straw

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HIGHLIGHTS

- The distribution of the volatiles in pyrolysis oil has been investigated.
- The effect of low-boiling volatiles on the bio-oil stability has been determined.
- The changes of active small molecules in low-boiling volatiles have been studied.
- A mechanism has been proposed to understand the ageing process of pyrolysis oil.

ARTICLE INFO

Article history:

Received 4 January 2015

Received in revised form

19 March 2015

Accepted 22 March 2015

Available online 2 May 2015

Keywords:

Pyrolysis oil

Atmospheric distillation

Stability

Volatiles

ABSTRACT

Because of the shortage of oil resources and the deteriorating environmental problems, the biomass fast pyrolysis oil deservedly offers an opportunity as alternatives to replace fossil fuels due to its renewable characteristics. However, pyrolysis oil is an unstable product and the physical and chemical properties are changing during storage, which limit its application. In this work, the volatiles changes in pyrolysis oil have been investigated by atmospheric distillation using constant temperature oil bath during an accelerated ageing process (store at 80 °C). Although the total volatiles contents of pyrolysis oil showed slight change during the accelerated ageing process, the variation of low-boiling volatiles with ageing time was evident. And fraction 1 (low-boiling volatiles) is one cause of the pyrolysis oil instability (based on the change in viscosity and water-insolubles). The chemical compositions of the low-boiling volatiles have been analyzed by gas chromatography/mass spectrometry and the variations of nine typical active small molecules in low-boiling volatiles over ageing time have been illustrated. Furthermore, a plausible mechanism based on the composition variation of pyrolysis oil (emphatically investigated solids and active molecules) has been proposed to illustrate the ageing process of pyrolysis oil for this study, suggesting that solids had synergy with active molecules to promote the pyrolysis oil condensation degree.

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1. Introduction

Bio-oil from biomass fast pyrolysis has aroused extensive attention and is regarded as a promising renewable fuel due to fossil fuel shortage and severe environmental problems. According to the Renewable Energy Directive, the renewable fuels should account for 20% of the EU's energy by 2020, and 10% bio-fuels are used as the transport sector (Commission, 2009). In the United States, the US Department of Energy Biomass Program provided fund of USD 385 M to support six large-scale bio-fuel plants to produce a total of over 500 Ml/yr during 2007. And Canada created

a USD 500 M fund to invest in private companies developing large-scale facilities for producing bio-fuel (Sims et al., 2010).

Unfortunately, compared to mineral oil, the bio-fuel, derived from biomass fast pyrolysis, is not a product of thermodynamic stability. So far, more than 300 compounds have been detected in fast pyrolysis oil, which comprise both polar and non-polar chemicals with multi-functional groups, such as aldehydes, ketones, alcohols, acids, esters, sugars, furans, phenols, guaiacols, syringols, lignin derived phenols and extractable terpene (Czernik and Bridgwater, 2004; Lu et al., 2011; Zhang et al., 2007).

During storage, the physical and chemical properties of the bio-oil were continuously changing and slowly tended to be stable. The instability of pyrolysis oil can be observed as the gradually increase in the water content, viscosity, the water-insoluble fraction and molecular weight with time (Oasmaa and Kuoppala, 2003). It is mainly because of the complicated chemical reactions

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in the pyrolysis oil, for example, the esterification reaction of organic acids with alcohols, condensation reactions involving aldehydes, ketones, alcohols, phenols, furfurals, and water (Onay and Koçkar, 2006). Then, these ageing reactions lead to the variations of the polarity and solubility of bio-oil. Esterification reactions convert highly polar organic acid and alcohol molecules into relatively low polarity esters and extremely polar water, and polymerization reactions generate large molecules that have limited mutual solubility with water in bio-oils (Lu et al., 2009). Although the increased water would reduce the viscosity, this effect is overwhelmed by an increase in the heavy water-insoluble fraction (Talmadge et al., 2014). In addition, the low-boiling volatiles of bio-oil are converted to large molecules by chemical reactions, which also lead to the change in the boiling point distribution of bio-oil. The chemical and physical instability of pyrolysis oil limit its direct application. Therefore, it is necessary to assess the stability of pyrolysis oil.

Accelerated aging experiments are often applied to investigate the stability of pyrolysis oil (Alsobou and Helleur, 2014; Elliott et al., 2012; Hilten and Das, 2010). The variation in viscosity of bio-oil stored at 80 °C for 24 h is equivalent to that stored at room temperature for 1 year (Oasmaa and Kuoppala, 2003). The test method based on viscosity change was widely used to determine the storage stability of bio-oil. On considering the instability of carbonyl compounds in bio-oil, a simple stability test method based on changes in aldehydes and ketones has been established (Oasmaa et al., 2011). Moreover, several parameters were applied to assess the stability of bio-oil, including water content (Zhang et al., 2013a), pH (Kim et al., 2012), solid content (Javaid et al., 2010), and average molecular weight (Eide et al., 2006).

The objectives of this study were (1) to investigate the influence of ageing time on the volatiles by atmospheric distillation and (2) to determine the effect of low-boiling volatiles on the stability of pyrolysis oil. Furthermore, a mechanism was put forward to illustrate pyrolysis oil ageing process according to the composition variation of pyrolysis oil.

2. Experiment

2.1. Rice straw bio-oil and accelerated ageing process

The rice straw pyrolysis oil used in this study was kindly provided by Shaanxi Yingjiliang Bio-energy Corporation, China. The bio-oil was produced in a downstream circulating fluidized bed reaction by flash pyrolysis of rice straw, which was collected from local farmland. And the pyrolysis liquid was obtained with high heating rate (approximately 500 °C/s), at moderate reaction temperature (about 500 °C) and with short vapor residence time (a few seconds) and low reaction pressure (1.5–2.2 kPa). The yield of oil, gas, and char product was 45, 22, and 33 wt%, respectively.

For accelerated ageing experiments, approximately 80 mL of the samples were poured into 100 mL sealed dry glass bottles. Then, the bottles were placed in a heating oven at 80 °C (± 1 °C) for 24 h, 48 h, 72 h and 96 h. In order to ensure no weight loss during accelerated ageing process, the vials must be weighed before and after ageing. After that, the evenly blended samples were tested and analyzed.

2.2. Atmospheric distillation

Approximately 20 g of the samples were poured into a round-bottom flask, which were heated with an oil bath at a series of constant temperatures under vigorous magnetic stirring. In this atmospheric distillation, the oil bath was kept at a certain temperature for 30 min and the condensed vapors were collected

Table 1
Experimental conditions during bio-oil distillation.

Distillate fraction	Heating temperature (°C)
Fraction 1	140
Fraction 2	180
Fraction 3	220
Fraction 4	250

continually before the round-bottom flask was cooled to room temperature. Table 1 showed the fractions collected at various heating temperatures.

2.3. Solvent extraction

In the solvent extraction experiment (Oasmaa and Kuoppala, 2003, 2008), the water-solubles and water-insolubles could be obtained by adding water in the pyrolysis oils (oil:water=1:10, v:v). The water-solubles were further divided into ether-soluble and ether-insoluble fractions by the diethyl ether extraction (the water-solubles:diethyl ether=1:1, v:v).

2.4. Bio-oil analysis

The bio-oil was analyzed for the water content, kinematic viscosity, density, pH, solid content, extractive, ash content, and heating value and elemental composition.

Water content: Karl–Fischer titration technique (AKF-1, Shanghai Hogon Instrument Factory, China) was applied to measure the water content. The titration solvent was a mixture of methanol and chloroform with the mass ratio of 3:1. In order to guarantee the accuracy of experimental results, the distilled water was used for calibration experiment.

Kinematic viscosity: the kinematic viscosity of the bio-oil samples was measured by a glass capillary viscometer. The measured temperature was constant at 40 °C and the standard reagent was used to obtain the constant factor of the viscometer.

Density: the density of bio-oil was determined by a density bottle.

pH: the pH value was measured by a pH probe with a digital meter (pHS-25, Shanghai Leici Instrument Plant). Buffer solutions of pH 4.0 and 6.86 were used to calibrate the instrument before the analysis.

Solid content: the solid content was determined as the methanol/dichloromethane insoluble materials using a vacuum filtration technique. This method was shown elsewhere (Lu et al., 2008).

Extractives: extractives were determined as n-hexane-soluble material. This method was recommended by Oasmaa et al. (2002).

Ash content: the residue was calculated as ash content after bio-oil was burned in a furnace at 775.8 °C for 24 h.

Heating value: the higher heating value (HHV) was calculated using the following equations (Pattiya and Suttibak, 2012; Sheng and Azevedo, 2005):

$$\text{HHV}(\text{MJ}/\text{kg}) = -1.3675 + 0.3137C + 0.7009H + 0.0318O \quad (1)$$

where, C and H are the percentages on dry basis of carbon and hydrogen, respectively and O is calculated by difference

$$O(\%) = 1 - C(\%) - H(\%) - N(\%) - \text{ash}(\%)$$

Element analysis: the elemental analysis of the pyrolysis oil was conducted on a vario micro cube elemental (Elementar, Germany). The C, H, N and S contents can be measured directly and the oxygen content was calculated as the difference: $O(\%) = 1 - C(\%) - H(\%) - N(\%) - S(\%)$.

The chemical composition analysis: GC–MS analysis was done using Shimadzu QP2010Plus, with the following parameters:

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