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Storage performance of bio-oil after hydrodeoxygenative upgrading with noble metal catalysts

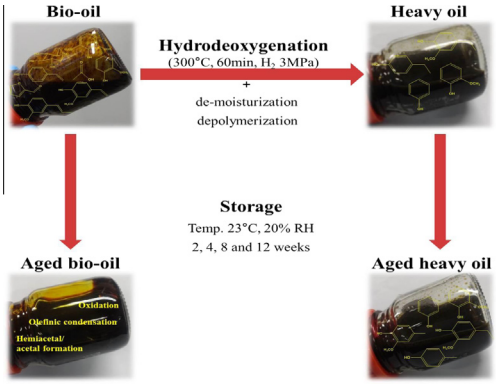
Shinyoung Oh [a], Hang Seok Choi [b], Ung-Jin Kim [c], In-Gyu Choi [a], Joon Weon Choi [d,*]

[a] Department of Forest Sciences and Research Institute for Agriculture and Life Science, Seoul National University, 599 Gwanak-ro, Gwanak-gu, Seoul 151-921, Republic of Korea
[b] Department of Environmental Engineering, Yonsei University, Wonju 220-710, Gangwondo, Republic of Korea
[c] Department of Plant & Environmental New Resources, College of Life Science, KyungHee University, Yongin-si, Kyunggi-do 446-701, Republic of Korea
[d] Graduate School of International Agricultural Technology and Institute of Green-Bio Science and Technology, Seoul National University, Pyeongchang 232-916, Gangwon-do, Republic of Korea

HIGHLIGHTS

- Upgraded heavy oil (HDO with Pd/C, Ru/C and Pt/C) was stored for 12 weeks.
- Properties of heavy oil were hardly varied during storage period.
- Hydrodeoxygenative process may effectively improve the stability of bio-oil.
- Degree of unsaturation showed that heavy oil retained stability during the storage.

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this study was to investigate the improvement in bio-oil stability via hydrodeoxygenation (HDO) with noble metal catalysts. The bio-oil produced by fast pyrolysis was subjected to the hydrodeoxygenative upgrading process with Pd/C, Ru/C, or Pt/C at 300 °C for 60 min with 3 MPa H_2 pressure. Upgraded bio-oil (heavy oil) was stored in sealed glass bottles at 23 °C for 2, 4, 8, or 12 weeks.

The major properties (water content, viscosity, and acidity) of heavy oils after storage and the chemical features (elemental composition and functional groups) of phenol polymers in the aged heavy oil were characterized.

Most properties of the aged heavy oil were maintained at the initial levels during the storage period, which indicates that the oil properties were stabilized by HDO. The water content slightly increased from 0.3–2.1 wt% to 2.3–3.5 wt% during the storage, but the viscosity and acidity of the oil hardly changed. Chemical compositions of low-molecular weight compounds in the aged heavy oils were slightly modified during storage. A slight increase in molecular weight was also observed and was attributed to partial repolymerization of phenol polymers in the heavy oil during storage. Overall, this study suggests that HDO upgrading effectively improves the stability of bio-oil properties.

* Corresponding author.
E-mail address: cjw@snu.ac.kr (J.W. Choi).

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1. Introduction

Liquid fuel is required to have homogeneous and stable properties during storage or at the generation facility. One alternative energy source, bio-oil, is considered to be a promising fuel for power generation systems and combined heat and power systems [1–3]. However, the large amounts of volatiles and many reactive oxygenated compounds including acids, aldehydes, sugars, and alcohols in bio-oil produce a glue-like material when stored for extended periods at ambient temperature, which leads to instability [4–7]. Moreover, polymerization, esterification, and etherification of these compounds can increase the viscosity of the bio-oil during storage, resulting in injection problems when used as a biofuel [1]. Therefore, maintenance and improvement of the properties and stability of biofuels are the main factors regarding their introduction into the market [8]. Catalytic treatments have been pursued to improve the composition of bio-oil. Many previous studies have investigated various upgrading processes, including hydrodeoxygenation (HDO), to significantly improve the stability of bio-oil [9–15]. In general, HDO is a low-hydrogen consumption process compared with other hydroprocesses as well as a method for manufacturing a more useful product from bio-oil [16]. Furthermore, the process is effective in stabilizing pyrolytic lignin, which makes up approximately 20% of bio-oil, and in enhancing bio-oil stability with supercritical ethanol [17,18]. Thus, modification of pyrolytic lignin and oxygenated compound during storage might be accomplished for assessing bio-oil stability.

Diebold [8] presented diverse chemical reactions expected to occur in bio-oil via the catalytic reaction, but these reactions also occurred in the absence of catalysts when bio-oil was stored at room temperature for a long time. Chemical reactions such as esterification of acids with alcohols, aldehyde polymerization, hydration of aldehydes or ketones with water, hemiacetal or acetal formation between aldehydes and alcohols, resin formation from aldehydes and phenols, olefin condensation, oxidation of alcohols and aldehydes to form carboxylic acids, and oxidative esterification of aldehydes were suggested to occur in bio-oil during storage [7,8]. These reactions are involved in property changes such as viscosity. Maintaining a lower viscosity is important for atomization and injection. Therefore, studies have been performed to experimentally demonstrate the occurrence of the above reactions [7,19]. As the storage effect of upgraded oil had not been generally proposed, in this study, the improved stability of bio-oil after hydrodeoxygenative upgrading was investigated. For this purpose, heavy oil, bio-oil upgraded via the hydrodeoxygenative process, was distributed in glass bottles and stored at 23 °C for 2, 4, 8, or 12 weeks. After storage, characterization of the stored heavy oil properties and the amounts of pyrolytic lignin were analyzed.

2. Material and methods

2.1. Hydrodeoxygenation upgrading of crude bio-oil

Crude bio-oil was produced from miscanthus biomass (*Miscanthussinensis*) using a fluidized-bed reactor [20]. Hydrodeoxygenation upgrading of crude bio-oil was performed at 300 °C for 60 min under 3 MPa H_2 pressure with three different noble metal catalysts (Pd/C, Ru/C, and Pt/C). After the reaction, the four main products – gas, char, and two immiscible liquids [aqueous phase (light oil) and organic phase (heavy oil)] were obtained and heavy oil was subjected to an aging test. Details of the hydrodeoxygenation process and heavy oil properties were reported in a previous study [20].

2.2. Aging tests of heavy oil

2.2.1. Storage of heavy oil

Previous studies have suggested that bio-oil has a low thermal stability, and an increase in temperature had a similar effect on bio-oil viscosity as storage [21,22]. However, thermal aging of oil might involve other properties or depend on the composition. Therefore, for stability testing, heavy oil was stored under fixed conditions (23 °C, 20% relative humidity) for 2, 4, 8, or 12 weeks. Heavy oils (obtained with HDO catalysts of Pd/C, Ru/C, or Pt/C) were weighed (25 g), placed in glass vials for each storage period, and tightly sealed with a plastic cap. Since bio-oil obtained from pine and oak wood showed stable viscosity for 60 days [7], heavy oils were stored for 3 months (84 days) to assess the role of aging on the stability of the oil. The weight of heavy oil was measured every two weeks for the first month and then monthly for the remainder of the storage period in order to determine the amount of lost volatile compounds.

2.2.2. Physicochemical properties

Typical physicochemical features of aged heavy oil including water content, pH, TAN (total acid number), and viscosity were measured after 2, 4, 8, or 12 weeks of storage in order to investigate the effect of HDO on heavy oil stability. Karl-Fischer titration (Titro Line KF, Schott Instruments, Germany), and a capillary-type viscometer and ViscoClock (Schott Instruments) at 40 °C were used to measure the water content, and viscosity of aged heavy oil, respectively. Also, the total acid number (TAN) of aged heavy oil was measured by an ASTM D664 method. Elemental analysis of carbon, hydrogen, and nitrogen was carried out with a LECO CHNS-932 analyzer. From the elemental analysis, the atomic H/C and O/C ratios were calculated; the degree of unsaturation was calculated using the following equation.

$$\text{Degree of unsaturation} = \text{Cm} + 1 - (\text{Hm} - \text{Nm})/2$$

where Cm, Hm, and Nm are the molar quantities of carbon, hydrogen and nitrogen, respectively. The degree of unsaturation was not affected by the oxygen content. The higher heating value (HHV) was calculated by Sheng and Azvedo's formula [23].

The average molecular weight of heavy oil before and after aging was measured using a GPC max instrument (ViscotekRImax, Viscotek, UK) coupled with a UV–Vis detector (VE3210, Viscotek) equipped with a PLgel 5 μm MIXED-C column (300 × 7.5 mm, Varian, Inc.) and a PLgel 5 μm guard column (50 × 7.5 mm, Varian, Inc.). Each 2 mg sample was dissolved in 2 ml tetrahydrofuran (THF) and filtered through a 0.5 μm hydrophobic syringe filter to remove insoluble solids. Polystyrenes with masses ranging between 580 Da and 3250 kDa were used as standards to create a calibration curve.

2.2.3. Identification of low-molecular weight components

To investigate the modification of low-molecular weight components (micro-molecules) in heavy oil during storage, qualitative and quantitative analyses of micro-molecules in heavy oil were performed using GC/MS. For this analysis, 50 μl internal standard (fluoranthene 25 mg/ml acetone) was added to 450 μl oil for quantitative analysis. The amount of micro-molecules in heavy oil during the storage period was calculated using the following equation.

$$\text{Amount of compounds(mg/ml oil)} = \text{Rf} \times A_{\text{compound}}/A_{\text{I.S}} \times M_{\text{I.S}} \times V_{\text{oil}} \times Y_{\text{heavy oil}}/100,$$

where Rf (response factor) depends on the type of compound; A_{compound} and $A_{\text{I.S}}$ are the area of the compounds and the area of the internal standard (I.S.), respectively; $M_{\text{I.S}}$ is the amount of added I.S. (mg), V_{oil} is the quantity of oil used in the analysis (ml), and