



Upgrading low-boiling-fraction fast pyrolysis bio-oil using supercritical alcohol: Understanding alcohol participation, chemical composition, and energy efficiency



Heuntae Jo^a, Hermawan Prajitno^b, Hassan Zeb^b, Jaehoon Kim^{a,b,*}

^a School of Mechanical Engineering, Sungkyunkwan University, 2066, Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 16419, Republic of Korea

^b SKKU Advanced Institute of NanoTechnology (SAINT), Sungkyunkwan University, 2066, Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 16419, Republic of Korea

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ABSTRACT

Herein, a supercritical methanol (scMeOH) route for efficient upgrading of the low-boiling fraction of fast pyrolysis bio-oil containing a large amount of low-molecular-weight acids and water was investigated. The effects of various reaction parameters, including the temperature, concentration, and time, were explored. The yield of bio-oil and the energy efficiency of the scMeOH upgrading process were determined based on the amount of methanol that participated in the reaction during upgrading and fractionation of the upgraded heavy-fraction bio-oils (UHBOs) and upgraded light-fraction bio-oils (ULBOs). Upgrading at 400 °C with 9.1 wt% bio-oil for 30 min generated a high bio-oil yield of 78.4 wt% with a low total acid number (TAN) of 4.0 mg-KOH/g-oil and a higher heating value of 29.9 MJ kg⁻¹. The energy recovery (ER) was 94–131% and the energy efficiency (EE) was in the range of 79–109% depending on the calorific values of the ULBOs. Compared with upgrading in supercritical ethanol and supercritical isopropanol, less alcohol participation, a lower TAN, and higher ER and EE were achieved with scMeOH upgrading. Plausible pathways for bio-oil upgrading in supercritical alcohols based on detailed compositional analysis of the UHBO, ULBO, and gaseous products were discussed.

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1. Introduction

Because of recent concerns about global warming and rapid fossil fuel depletion, biomass has received considerable attention as a sustainable and carbon-neutral resource for producing renewable fuels and chemicals [1–3]. Conversion of lignocellulosic biomass, a second-generation biomass feedstock, to renewable fuels is not plagued by concerns about the fuel vs. food competition, which is the main drawback of first-generation biofuels (e.g., corn-to-ethanol, natural triglyceride-to-biodiesel). There are several ways to convert lignocellulosic biomass to energy and fuel, which include combustion, gasification, hydrothermal liquefaction, and fast pyrolysis [4–6]. Among these techniques, fast pyrolysis is considered a highly promising and relatively scalable technique for producing liquid fuels from a variety of feedstocks (grass, trees, and organic wastes) because of its simplicity and low processing cost [7–10]. A moderate yield of bio-oil (50–80 wt%) can be

achieved at reaction temperatures of 500–600 °C with a very short reaction time of less than 5 s [11].

However, the physicochemical properties of the bio-oil produced from fast pyrolysis are very poor, which make fast pyrolysis bio-oil unsuitable for direct use as a combustion or transportation fuel [7,8,11–13]. For example, fast pyrolysis bio-oil has a large amount of oxygen-containing species such as acids, aldehydes, ketones, phenols, furans, and levoglucosans; the oxygen content is in the range of 35–40 wt% [13]. In particular, low-molecular-weight acids (such as formic acid and acetic acid) are highly reactive and give rise to many undesirable properties such as polymerization upon heating and instability during storage and transportation [14,15]. In addition, the low-molecular-weight acids are highly corrosive, and thus expensive anti-corrosive equipment and harsh downstream processing conditions are required. The highly-oxygenated compounds, such as furans and levoglucosans, lower the calorific value of bio-oil (e.g., the higher heating values (HHVs) are in the range of 15–20 MJ kg⁻¹) [13,16,17]. In addition, the high water content in the produced bio-oil increases the ignition delay and induces phase separation between the organic and aqueous phases [18]. The poor volatility caused by heavy fractions, the formation of re-polymerized prod-

* Corresponding author at: School of Mechanical Engineering and SKKU Advanced Institute of NanoTechnology (SAINT), Sungkyunkwan University, 2066, Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 16419, Republic of Korea.

E-mail address: jaehoonkim@skku.edu (J. Kim).

ucts during storage [19], and the immiscibility with fossil-derived fuels [13] make direct use of the “crude” bio-oil as a fuel difficult. Therefore, the development of proper upgrading techniques for decreasing the oxygen-containing species, increasing the calorific value, and stabilizing bio-oil is highly required for ultimate utilization of fast pyrolysis bio-oil.

Several upgrading techniques have been developed to improve the physicochemical properties of fast pyrolysis bio-oil. These include hydrogenation [20–22], hydrodeoxygenation [23–25], catalytic cracking [26,27], esterification [28–30], emulsification [31,32], and catalysis in supercritical fluids [33–36]. In the presence of external molecular hydrogen and catalysts (e.g., sulfide CoMo-, NiMo-, and noble metal- (Ru, Pd, Pt, etc.) supported catalysts, acid-impregnated silica, and acidic/basic metal oxides), effective hydrodeoxygenation and hydrocracking has been achieved, with reduction of the oxygen content and depolymerization of the high-molecular-weight species (e.g., pyrolytic lignin) in the bio-oil. Depending on the bio-oil sources, reaction media, and catalysis conditions, the upgraded oil had an oxygen content in the range of 15–36 wt% and a HHV in the range of 20–35 MJ kg⁻¹ [17]. However, the high consumption of expensive hydrogen and deactivation of the catalysts due to coking and inorganic impurities (e.g., Si, K, Fe, Al, etc.) and water [37,38] make catalyst-based upgrading processes less economically viable.

Recently, we proposed a supercritical ethanol-based approach for upgrading heavy-fraction fast pyrolysis bio-oil without using external hydrogen and catalysts. The hydrogen derived from the decomposition of supercritical alcohol in the hydride form [39] or proton transfer [40,41] and the unique reactivity of supercritical alcohols (e.g., esterification [42], alkylation [43,44], hydroxyalkylation [39,45], deoxygenation [46,47]) can result in effective reduction of the oxygen content, cracking of pyrolytic lignin, and suppression of re-polymerization. For example, a high-yield of upgraded oil (83.0 wt%) with a high HHV of 34.1 MJ kg⁻¹ and a low total acid number (TAN) of 4.8 mg KOH g⁻¹ could be achieved in scEtOH at 400 °C. Even though the previous work demonstrated the great potential of scEtOH-based upgrading, the utilization of scEtOH as the reactant raises several critical questions. (1) Although renewable ethanol can be produced by monosaccharide fermentation, ethanol is currently used as a transportation fuel and is much more expensive than methanol. In this context, can we develop an effective upgrading process using supercritical methanol? (2) During bio-oil upgrading, supercritical alcohol, as the hydrogen source and the reactant, will participate in the reaction. How much alcohol will be consumed during bio-oil upgrading? (3) Does the alcohol participation have a significant effect on the energy balance of the upgrading process, such as the energy recovery (ER) and energy efficiency (EE)? (4) Is supercritical alcohol-based upgrading effective for light-fraction fast-pyrolysis bio-oil containing a large amount of water?

In this study, we aim to develop an economically viable, supercritical methanol (scMeOH)-based upgrading technique and determine the feasibility of addressing the issues raised in the questions above. To gain comprehensive understanding of the energy balance of the non-catalytic and non-external hydrogen upgrading process, a new separation protocol was developed to estimate the amount of alcohol consumed during the upgrading and recovery of upgraded light-fraction bio-oils (ULBOs), which were typically evaporated and were not considered in most previous studies. Based on the alcohol consumption and the recovery of the ULBOs, new definitions of the bio-oil yield, ER, and EE are proposed. Upgrading at 400 °C with 9.1 wt% bio-oil for 30 min in scMeOH allowed achievement of a high bio-oil yield of 78.4 wt%, a significant reduction of the TAN from 92.2 to 4.0 mg-KOH/g-oil, a high ER of 94%, and an EE of 79% (under the assumption that the HHV of the ULBOs is 20.0 MJ kg⁻¹). The effect of the supercritical alco-

hol, reaction time, and bio-oil concentration on the yields and properties of the upgraded bio-oil are discussed in detail. In addition, the detailed chemical compositions of the upgraded heavy-fraction bio-oils (UHBOs) and ULBOs produced in scMeOH under varying reaction conditions are presented. Based on compositional analysis of the UHBOs and ULBOs, plausible upgrading mechanisms are proposed.

2. Experimental

2.1. Materials

The bio-oil used in this study was produced with a pilot-scale, fast pyrolysis apparatus using empty palm fruit bunch as the ligno-cellulosic biomass feedstock. Two separation units were installed in the downstream of the fast pyrolysis apparatus to recover the high-boiling-point fraction (HBF) bio-oil at around 150 °C and low-boiling-point fraction (LBF) bio-oil at around 70 °C. In this study, the low-boiling-fraction oil was used as the upgrading feedstock. Table 1 lists the properties of the fast pyrolysis bio-oil used in this study. Prior to the upgrading reaction, the low-boiling-fraction oil was stored in a refrigerator to avoid the aging effect [14,15]. HPLC-grade methanol, ethanol, and isopropyl alcohol, and acetone were purchased from Honeywell Burdick and Jackson® (USA). For the TAN and water content measurements, toluene (EP grade, Daejung Chemical & Metals Co., South Korea), deionized water (HPLC grade, Wako Pure Chemical Industries, Ltd., Japan), and Hydranal®-Composite 5 (Sigma-Aldrich Co., USA) were used. High-purity nitrogen (99.999%), helium (99.999%), and air (99.999%) were purchased from JC Gas Company (South Korea).

2.2. Upgrading reaction

A custom-built, SUS 316 reactor with an inner volume of 140 mL was used for the upgrading reaction in the supercritical alcohols. The reactor was equipped with a magnetic stirrer and two heating sources (cartridge heaters and a heat furnace). A detailed description of the reactor system used in this study is given elsewhere [17]. After loading the reactor with a known amount of the fast pyrolysis bio-oil and alcohol, the reactor was sealed and purged with N₂ several times by using the purge line dipped into the reactor in order to remove dissolved oxygen in the liquid phase and the oxygen in the reactor head. After purging, the reactor was pressurized with N₂ at 1 MPa and the stirring rate was fixed at 500 rpm. The reactor was then heated to the desired experimental temperatures at an average heating rate of 15 °C min⁻¹. After the desired reaction time, the reactor was water-quenched to a temperature of 100 °C and then cooled to room tem-

Table 1
Characteristics of the LBF bio-oil used in this study.

	LBF bio-oil
Water content (wt%)	23.7
Ash content (wt%) ^a	<0.01 wt%
TAN (mg-KOH/g-oil)	92.2 ^b
C (wt%)	42.5
H (wt%)	4.7
N (wt%)	N.D. ^c
S (wt%)	N.D. ^c
O (wt%)	41.7
HHV (MJ kg ⁻¹)	12.5

^a Calculated using TGA.

^b Calculated using Eq. (9).

^c N.D.: No detected because of detection limit of the EA (below 0.01 wt%).

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