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Non-catalytic upgrading of fast pyrolysis bio-oil in supercritical ethanol and combustion behavior of the upgraded oil

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HIGHLIGHTS

- Non-catalytic, non H_2 bio-oil upgrading was conducted in supercritical ethanol.
- High HHV of 34.1 MJ kg^{-1} and low TAN of 4.8 mg KOH/g were achieved.
- Alcohol and ester species were the major compounds in the upgraded oil.
- Upgraded oil exhibited excellent thermal stability and low viscosity.
- Upgraded oil firing exhibited high total heat transfer rate of 121.81 MW_{th}.

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ABSTRACT

Fast pyrolysis bio-oil derived from empty palm fruit bunch was upgraded in supercritical ethanol (scEtOH) without using external catalysts and molecular hydrogen. The effects of the reaction temperature and time on the product yield and the quality of the upgraded oil based on parameters like the elemental content, total acid number (TAN), water content, high heating value (HHV), and viscosity were examined. At 400 °C, almost all of the organic species in the fast pyrolysis bio-oil were converted to the liquid and gas phase in 30 min, resulting in a high yield of the upgraded oil (83.0 wt%) with an enhanced HHV of 34.1 MJ kg^{-1} and very low values of TAN (4.8 mg KOH g^{-1}) and water (1.6 wt%) when compared to the fast pyrolysis bio-oil (HHV, 24.3 MJ kg^{-1}; TAN, 69.4 mg KOH g^{-1}; water, 14.0 wt%). The major chemical species in the upgraded oil were alcohols, esters, phenols, hydrocarbons, and aromatics. After aging at 80 °C for one week, a marginal increase in the viscosity of the upgraded bio-oil was observed, indicating a significant improvement in the stability of the bio-oil. Computational fluid dynamics (CFD) analysis of the process performed in a commercial boiler demonstrated that the upgraded oil firing exhibited high gas temperature profiles, a high firing peak of 1599 °C, and a high total heat transfer rate of 121.81 MW_{th}. These results are comparable to the performance parameters of conventional heavy oil-firing processes.

1. Introduction

Bio-oil produced from lignocellulosic biomass is one of the most promising clean and renewable energy resources with the potential to overcome problems associated with rapid fossil fuel depletion, global warming and food vs. fuel competition. This field has received considerable attention due to the environment friendly characteristics of bio-oil such as zero net CO_2 emissions with regard to carbon circulation, low emission of polluting gases during its utilization and high sustainability of its production [1–4]. Fast pyrolysis is a simple and relatively low-cost technique to convert lignocellulosic biomass to liquid fuels with moderate liquid yields (50–80 wt%) when compared to other thermochemical conversion approaches [5].

However, the bio-oil produced using fast pyrolysis often exhibits undesirable properties such as high moisture content, high oxygen content, and high reactivity caused by the presence of substantial amount of oxygenated and unsaturated compounds, which limits its utilization as combustion or transportation fuels. For example, the presence of large amounts of aldehydes and phenolic species in the fast pyrolysis bio-oil leads to an unstable product

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because these species tend to polymerize quite easily [6,7]. This leads to an increase in the oil viscosity and changes its properties in an unpredictable manner, which makes transportation and further downstream processing difficult. The presence of high moisture and oxygenated compounds in fast pyrolysis bio-oil results in low heating values and immiscibility with conventional fossil fuels [8]. The inevitable presence of acidic compounds in the bio-oil results in a thermally unstable and highly corrosive oil [9,10]. Therefore, the development of an upgrading process for fast pyrolysis bio-oil to produce a high calorific value fuel with lower quantities of oxygen and acidic species is urgently required to achieve the ultimate goal of the partial or complete replacement of fossil fuels [11].

When compared with hydrothermal technique, upgrading of fast-pyrolysis bio-oil is very attractive to be developed because the fast-pyrolysis technology has been successfully commercialized by several companies worldwide. A recent study on techno-economic analysis of hydrothermal liquefaction combined with catalytic upgrading revealed high production cost of biofuel [12]. Until recently, a wide variety of techniques has been explored for the upgradation of fast pyrolysis bio-oil, as summarized in Table S1. Hydrogenation is one of the widely used methods to upgrade fast pyrolysis bio-oil. It exploits molecular hydrogen and heterogeneous catalysts to reduce the oxygen content, saturate olefins, and to convert aromatics into cycloalkanes [2]. However, the upgraded oil retains a low higher heating value (HHV, 14 MJ kg^{-1}) and a low pH value (2.5–2.8) (see Table S1) [13–15]. In addition, catalyst deactivation by coke deposition is another major drawback of this process. Hydrodeoxygenation using catalysts such as sulfided CoMo- and noble metal- (Pd, Pt, Ru, etc.) supported catalysts or catalytic cracking using zeolite-based catalysts is an effective method to decrease the oxygen content (2–31 wt%) of bio-oils. Nevertheless, complicated reaction systems, high upgrading costs, catalyst deactivation and reactor clogging issues need to be addressed for the effective implementation of this process [2,16–21]. Besides, a direct upgrading process after pyrolysis using two-stage reactor (a pyrolyzer and catalytic reformer) with nickel phosphide and HZSM-5 catalyst brought to a lowered bio-oil yield (8–27 wt%) compared with that of non-catalytic approaches (27–34 wt%) [22,23]. Esterification of acidic species using alcohols is an alternative way to upgrade fast pyrolysis bio-oil. This approach is especially beneficial because the plentiful amounts of carboxylic acids present in most fast pyrolysis bio-oils is the primary factor responsible for the acidity observed in these cases. However, the quality of the upgraded oil is still unsatisfactory even when additional molecular distillation or hydrotreatment processes (HHV of 14–31 MJ kg^{-1}, oxygen content of 28–39 wt%) were applied [8,24–35].

Upgrading fast pyrolysis bio-oil in supercritical alcohols is considered a potential alternative due to the unique properties of supercritical fluids: the gas-like properties (high diffusivity and low viscosity) and the liquid properties (high density), faster rates of mass and heat transfer, and good dissolving power [9,20,36–44]. In most of the previous studies, supercritical alcohol was used as a solvent and an esterification reagent, and precious metal- supported catalysts (Pt, Pd, or Ru supported on carbon, zeolites, acid-impregnated silica, etc.) or acidic/basic metal oxide- based catalysts and external molecular hydrogen were used for enhancing the hydrodeoxygenation and/or cracking reaction to convert the oxygenated species and high-molecular-weight species (e.g., pyrolytic lignin) present in the crude bio-oil. Depending on the reaction time (60–480 min) and reaction temperatures (80–370 °C), the upgraded oil exhibited HHV in the range of 20–35 MJ kg^{-1} and oxygen content in the range of 14–36 wt%, indicating that the catalytic reaction in supercritical alcohol could be an alternative fast pyrolysis bio-oil upgrading approach. However, the high upgrading costs associated with the precious metal supported catalysts and external molecular hydrogen would not meet the current demand for producing combustion or transportation fuel in an economically viable way. In addition, most of the fast pyrolysis bio-oils contain significant amount of inorganic impurities (e.g., Si, K, Zn, Fe, Al, etc.), which will cause severe metal catalyst deactivation. Furthermore, the loss of catalyst activity caused by coke deposition on the active sites and catalyst sintering should be addressed for practical utilization of the catalytic bio-oil upgrading process. Therefore, non-catalytic upgrading would be a better choice if similar stabilization and oxygen removal effects can be implemented in this case. In spite of its clear advantages, only a few studies have reported non-catalytic upgrading of fast pyrolysis bio-oil [20,36,37]. The upgraded oil in these cases exhibited relatively poor physicochemical properties when compared to the catalytically upgraded oil. For example, Peng et al. reported that the upgraded oil in scEtOH at 260 °C and 7.8 MPa retained a low HHV of 20.1 MJ kg^{-1} and the acidic species present in the sample were not converted completely [36]. Tang et al. observed severe coke formation during the upgrading process in the subcritical state of ethanol at 280 °C and 0.5 MPa, and a very low HHV of 6.2 MJ kg^{-1} in the obtained bio-oil [37]. Later, Kim et al. reported that the use of ethanol at 350 °C resulted in increasing the HHV from 20.1 to 33.4 MJ kg^{-1}, but the upgraded oil still retained a high oxygen content of 18.6 wt% [20].

In this study, non-catalytic and non-external hydrogen upgrading of fast pyrolysis bio-oil in scEtOH was explored to examine the possibility of producing high calorific value oil with low oxygen content. An effective utilization of the unique hydrogen-donating ability associated with scEtOH involving both donation of an α-hydrogen in the hydride form [45] and proton transfer through the Meerwein–Ponndorf–Verley reduction mechanism [46], can be very effective in the depolymerization of high-molecular-weight species including pyrolytic lignin. This hydrogen-donating ability would also play a role in deoxygenation to improve the calorific value of upgraded oil, and in retarding repolymerization and tar formation [47]. In-situ hydrogen generation by dehydrogenation of alcohol to ethyl acetate may be ignorable in the absence of suitable catalysts [48]. In addition to the hydrogen generation, scEtOH is very effective in the non-catalytic esterification of carboxylic acids (e.g., free-fatty acids to produce biodiesel) [49]. Thus, the effective transformation of various types of acidic species in fast pyrolysis bio-oil to non-corrosive and less reactive ester species can be expected. These beneficial factors associated with scEtOH can suggest effective upgrading of fast pyrolysis bio-oil without using the precious metal-supported catalysts and external molecular hydrogen. Based on these it would be possible to develop a much simpler and less expensive upgrading process for the ultimate utilization of bio-oil. In our study on the feasibility of non-catalytic upgrading of bio-oil using scEtOH, the process parameters (reaction temperature and reaction time) were carefully controlled to produce high quality upgraded oil. As a result, an upgraded bio-oil with a yield of 83.0 wt%, a HHV of 34.1 MJ kg^{-1}, total acid number (TAN) of 4.8 mg KOH g^{-1}, and water content of 1.6 wt% was obtained, which have not been achieved previously in non-catalytic supercritical alcohol upgrading approaches. These values are comparable to or better than the previous catalytic upgrading results (see Table S1). The composition and aging of the upgraded oil was analyzed in detail. In addition, we first demonstrate the feasibility of complete or partial fuel switching of heavy fuel oil from petroleum resources to bio-derived oil for electricity generation; combustion and heat transfer characteristics of the fast pyrolysis bio-oil and the upgraded oil in a commercial 100 MW_e-capacity boiler was examined for the first time using computational fluid dynamics (CFD).