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 H2 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 MWth.

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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 \(^\circ\)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 \(^\circ\)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 \(^\circ\)C, and a high total heat transfer rate of 121.81 MWth. 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...
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 heat 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, olefins, and to convert aromatics into cycloalkanes [2]. The heterogeneity of the upgrading process for fast pyrolysis bio-oil, however, high HHV of 20.1 MJ kg⁻¹ and the acidic species present in the sample were not converted completely [36].

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 MWc-capacity boiler was examined for the first time using computational fluid dynamics (CFD).