



# Upgrading of syngas hydrotreated fractionated oxidized bio-oil to transportation grade hydrocarbons



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## ABSTRACT

Fast pyrolysis bio-oils have the potential to replace a part of transportation fuels obtained from fossil. Bio-oil can be successfully upgraded into stable hydrocarbons (gasoline, jet fuel and diesel) through a two-stage hydrodeoxygenation process. Consumption large amount of expensive hydrogen during this process is the major hurdle for commercialization of this technology. Applying syngas in the hydrotreating step can significantly reduce the cost of the whole process and make it competitive. In this study, four different models of syngas with different H<sub>2</sub> concentrations (H<sub>2</sub>/CO molar ratios = 2:8, 4:6, 6:4 and 8:2) were used for the 1st-stage hydrotreating step of oxidized fractionated bio-oil (OFB). The 2nd-stage hydrocracking step was performed on the produced organic liquid products (OLPs) by using pure H<sub>2</sub> gas. The effect of syngas H<sub>2</sub> concentrations on the yields and properties of OLPs and the 2nd-stage hydrocarbons (HCs) was investigated. Physical and chemical properties of the 2nd-stage hydrocarbons were similar regardless syngas H<sub>2</sub> content, with the exception of the viscosity. Syngas with H<sub>2</sub>/CO molar ratio of 4:6 gave significantly highest HCs yield (24.8 wt.%) based on the OFB. Simulated distillation analysis proved that all 2nd-stage hydrocarbons were mixture from a wide range boiling point fuels. These results also indicated that the successful 1st-stage syngas hydrotreating step was having the potential to produce different hydrocarbons.

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## 1. Introduction

Sustainable fast pyrolysis bio-oils have the potential to replace a proportion of energy currently obtained from fossil fuels [1]. Fast pyrolysis bio-oil exhibits a complex composition with water (~30 vol.%) as its predominant component and numerous reactive oxygenates in the form of esters, carboxylic acids, ethers, ketones, aldehydes, anhydrous saccharides, phenolic derivatives and aliphatic and aromatic alcohols. These oxygenates in the bio-oil cause most of the negative physical and chemical properties such as low heating value (~17 MJ/Kg), corrosiveness (~pH 2.5), immiscibility with fossil fuels and a tendency to polymerize and phase separation with time and/or exposure to temperature [2]. Moreover, carbonyl compounds such as aldehydes and ketones have been identified as chiefly responsible for coking reactions (thermal and catalyst coking) during hydroprocessing [3]. The presence of high water content is harmful to the acid  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or zeolite supports (dealumination), which are the main supports for deoxygenation in petroleum refining and bio-oil upgrading. This water-based oxy-

gen becomes steam vapor during thermo-chemical hydroprocessing and collapses the pores of catalysts [4]. Therefore, such properties severely limit fast pyrolysis bio-oils for direct use as an energy source and also cause significant challenges in the conversion of the bio-oil to hydrocarbon fuels.

It has been well known that hydrodeoxygenation (HDO) is able to remove oxygen and produce liquid hydrocarbons (HCs) in the presence of H<sub>2</sub> and heterogeneous catalysts [5]. To reduce bio-oil polymerization at high temperatures, previous researchers [6,7] developed a two-stage HDO process. Partial deoxygenation was accomplished in the 1st-stage at mild temperature to remove water and convert some oxygenated compounds to HCs. Polymerization of bio-oil and catalyst coking were limited due to the lower temperatures applied during this 1st-stage hydrotreating. With these changes, full deoxygenation was accomplished during the 2nd-stage at higher temperatures without product polymerization and the extremely rapid catalyst coking previously experienced for single-stage HDO. However, the two-stage HDO continues to be hampered with low hydrocarbon yields as well as by catalyst coking [6]. In addition, H<sub>2</sub> pressures applied for HDO have been relatively high ranging from 1510 to 3000 psig [2,8,9]. The high cost of H<sub>2</sub> for performing HDO has also been noted as a problem for

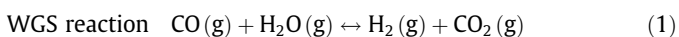
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commercialization. Technologies to reduce H<sub>2</sub> consumption would be required for the eventual economic commercialization of the HDO process.

Presence of high amounts of oxygen in the form of water and oxygenated reactive functional groups, and the needs for expensive upgrading methods to refine bio-oil have been the main road blocks for bio-oil to hydrocarbon fuel commercialization. Separation of water and reactive compounds before proceeding to HDO tends to limit thermal coking and catalyst coking encountered during the upgrading process [10]. Effective solvent fractionation methods have been developed to separate different bio-oil fractions from each other [11–13]. Fractionation of water and a portion of aqueous fraction from bio-oil organic components can also be achieved during pyrolysis itself [14–16]. These methods utilize temperature controlled multiple condensers of a pyrolysis reactor where the separation of pyrolysis vapor into each individual condenser occurs based on respective molecular weight classes. In addition to the application of temperature controlled coolants, selective condensation of fast pyrolysis vapors was also achieved using a liquid spray bio-oil [17] or water [18] to quench and fractionate pyrolysis vapors. The organic fractions with lower water content and anhydrosugars decomposition products have been shown to be catalyzed more effectively to produce hydrocarbon fuels and other products [19,20]. Marker and Petri [19] utilized an HDO method to produce hydrocarbons mixture containing aromatic and naphthenic compounds from the low-water organic phase of fractionated bio-oil. A two-stage catalytic hydroprocessing method was applied using mild hydrotreating at low temperature followed by hydrocracking at a higher temperature.

Tanneru and Steele [7] found that partial nickel/silica-alumina catalyzed HDO of raw bio-oil oxidized with oxone/H<sub>2</sub>O<sub>2</sub> lowered char production as well as reduced hydrogen consumption while producing 30.5% higher organic fraction yield compared to partial HDO of raw bio-oil. The oxidation step significantly changed the bio-oil chemical composition by converting aldehydes and ketones into carboxylic acid. Luo et al. [21] proved that the two-stage HDO of the oxidized fast pyrolysis fractionated bio-oil produced HCs yield of 20.5 wt.%, which was nearly 76% higher than that for raw bio-oil alone of 11.6 wt.%. Applying syngas in the hydrotreating step has some advantages over hydrogen. Syngas can be produced from the same renewable feedstock used to produce bio-oil. The cost of syngas produced from biomass is a cheaper (~0.3 cents/mole (CO + H<sub>2</sub>)) than pure hydrogen produced from catalytic steam reforming of methane (~0.5 cents/mole) [22,23]. Tanneru and Steele [24] successfully produced a hydrotreated 1st-stage product with improved physical and chemical properties by partial deoxygenation of oxidized raw bio-oil with one syngas composition of 18% CO. Hydrogen produced by the water gas shift (WGS) reaction (Eq. (1)) allowed the 1st-stage hydrotreating step to be completed successfully. However, these researchers were not successful in performing 2nd-stage hydrocracking by catalyzing their 1st-stage product in the presence of the same pressurized syngas. Researchers assumed that inadequate H<sub>2</sub> for the 2nd-stage hydrocracking was due to too low H<sub>2</sub>O (2.2 vol. %) in the 1st-stage hydrotreated products to participate in WGS reaction with CO (18–20%) in the syngas to produce adequate H<sub>2</sub> in addition to the original H<sub>2</sub> (19–22%) in the syngas. Therefore, Tanneru and Steele [24] found it is necessary to perform the 2nd-stage hydrocracking with H<sub>2</sub> to produce HCs with zero/low oxygen content.



The objective of this study was to evaluate the effect of H<sub>2</sub> content in the syngas of the 1st-stage hydrotreating step on the product yield and properties of the final hydrocarbon products produced after the 2nd-stage hydrocracking step. For this purpose, four different models of syngas with different H<sub>2</sub> concentrations

(H<sub>2</sub>/CO molar ratios = 2:8, 4:6, 6:4 and 8:2) were used in the 1st-stage hydrotreating step. The second hydrocracking step was performed by using pure H<sub>2</sub> to achieve full HDO.

## 2. Materials and methods

### 2.1. Materials

Nickel/silica-alumina (~65 wt.% nickel, powder, a surface area of 190 m<sup>2</sup>/g), copper oxide and potassium carbonate were purchased from Alfa Aesar (U.S.). Syngas (H<sub>2</sub>/CO molar ratios: 2:8, 4:6, 6:4, 8:2), hydrogen (H<sub>2</sub>) and helium (He) gases were supplied by NexAir (U.S.). Hydrogen peroxide (30 wt.% solution in water, Certified ACS 30.0–32.0%), isopropanol (99.9%, HPLC Grade), methanol (Stabilized/Certified ACS), dichloromethane (Stabilized/Certified ACS), and oxone were purchased from Fisher Scientific. All the chemicals were used without further purification.

### 2.2. Methods

#### 2.2.1. Preparation of fractionated bio-oil

Loblolly pine (*Pinustaeda*) was ground and sieved to a particle size range of 0.5–4 mm and then oven-dried to a moisture content below 5 wt.%. Fast pyrolysis experiments were performed in stainless steel auger reactor at a temperature of 450 °C. Full description for the fast pyrolysis process and the schematic representation for the reactor was explained briefly in our previous work [21]. The bio-oil organic fractions tended to be condensed in condensers 1, 3, 4 liquid condensates were collected from the exits of the first, third and fourth condensers and combined together to form the fractionated bio-oil (FB) which used for this study. Fractionated bio-oil relatively has low water content than raw bio-oil (RB) which can be collected from all four condensers. The second condenser bio-oil has relatively high water content than other condenser bio-oils because vapors tend to condense more in this condenser as it is maintained below the water vaporization temperature.

#### 2.2.2. Oxidation of fractionated bio-oil

The oxidation of the fractionated bio-oil was performed in a stainless steel, high-pressure 1.8 L Parr batch autoclave reactor equipped with an overhead magnetic stirrer, a maximum pressure capacity of 5000 psig and maximum temperate capacity of 500 °C. Oxidation of FB was performed by the same methods described by Tanneru and Steele [7] by the addition of 10 wt.% hydrogen peroxide and 5 wt.% oxone followed by stirring for 90 min at ambient temperature and pressure. The oxidized fractionated bio-oil was termed as (OFB).

#### 2.2.3. Hydrotreating and hydrocracking steps

Partial deoxygenation by a mild temperature hydrotreating 1st-stage was applied to the OFB with model syngas types comprised of four different H<sub>2</sub>/CO molar ratios (2:8, 4:6, 6:4 and 8:2). Catalytic reactions were performed in the 1.8 L Parr batch reactor by using 5 wt.% nickel/silica-alumina to catalyze the HDO reaction, and (2 wt.% copper oxide and 3 wt.% potassium carbonate) as a promotor to improve the performance of the catalyst toward WGS reaction. 1st-stage partial deoxygenation reactions were performed for 2 h at a temperature of 340 °C and an initial syngas pressure of 1000 psig. The 2nd-stage hydrocracking reactions were performed with pure H<sub>2</sub>. The catalytic hydrocracking step was performed in the presence of 10 wt.% nickel/silica-alumina for 2 h at a temperature of 400 °C and an initial H<sub>2</sub> pressure of 1000 psig. After each experiment, the reactor was cooled by water to the ambient temperature, and a gas sample was collected in a 1 L Tedlar gas

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