



## Full Length Article

# Effects of single-stage syngas hydrotreating on the physical and chemical properties of oxidized fractionated bio-oil



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## ABSTRACT

Previous research has shown that syngas can successfully hydrotreat bio-oil, but the hydrotreated products still had high viscosity, total acid number, oxygen content, etc. The current study was based on the hypothesis that higher temperature syngas hydrotreating may reduce the viscosity, total acid number, oxygen content and increase the total hydrocarbon concentration. In the current study, hydrotreating of oxidized fractionated bio-oil was performed at 400 °C in the presence of syngas (molar ratio H<sub>2</sub>: CO was 4:6). The total yield of the organic liquid product was 34.2 wt%, and 40 wt% of the total organic phase was composed of hydrocarbons (olefins, aromatics and polyaromatics). The treated bio-oil had upgraded physiochemical properties with a water content of 1.6 vol%, a higher heating value of 38.3 MJ/kg, a density of 0.96 g/mL, a viscosity of 12.2 cSt and a total acid number of 22.0 mg KOH/g. Functional group distinctions were detected by Fourier transform infrared spectroscopy and the chemical composition differences were identified by gas chromatography/mass spectrometry. The results indicated that the fractionated bio-oil had been greatly improved by syngas hydrotreating at 400 °C. This success of syngas hydrotreating at a higher temperature has the potential to allow the replacement of hydrogen with syngas for the partial upgrading of oxidized bio-oil.

## 1. Introduction

Previous research has shown that pyrolytic bio-oils can be converted into hydrocarbons suitable for transportation fuels [1–7]. However, a major problem with bio-oil includes its degradation during storage over time. Immediately after the production process is completed bio-oil begins to polymerize, and this polymerization continues to occur at a slow rate at room temperature. The polymerization is primarily caused by the presence of oxygenated reactive compounds that cause chemical linkages to form in the bio-oil [8–10]. Diebold summarized ten possible reversible and irreversible reactions of bio-oil due to aging with time, or upon heating, with seven of them related to the presence of aldehydes [11].

A centralized bio-oil facility should pyrolyze the biomass at regionally distributed processing facilities close to the biomass resource [12–14]. The bio-oil is transported to a more centralized bio-oil conversion facility where hydrogen is available. This reduces the high cost for biomass transportation by replacing it with lower-weight bio-oil transportation [15–17].

Loblolly pine (*Pinus taeda*) is the major species grown in the

southern U.S. Bio-oil conversion facilities built in the south have previously used small diameter loblolly pine as the biomass feedstock [18–20]. The actual reduction in shipment weight between green loblolly pine pulpwood is approximately 73% due to the removal of approximately 55% of the water content from the small-diameter loblolly pine prior to pyrolysis. Therefore, rather than shipping a ton of biomass over a long distance, the same shipment of bio-oil produced from that green ton would be approximately 540 lbs.

The replication of numerous hydrogen production facilities or shipping hydrogen to numerous distributed pyrolysis sites would not be economically feasible due to the high capital or variable shipment costs. However, the production of syngas from the gasification of biomass feedstock used for bio-oil upgrading is much less expensive than pure hydrogen production. Typically, hydrocarbons produced from bio-oil produced from a pyrolysis reactor are hydrotreated in one stage whereby the resulting organic liquid product (OLP) contains some hydrocarbons, a considerably lower water content, and lower oxygen content than raw bio-oil (RB).

Tanneru and Steele [21] have demonstrated that the oxidation of bio-oil significantly changed the bio-oil chemical composition by

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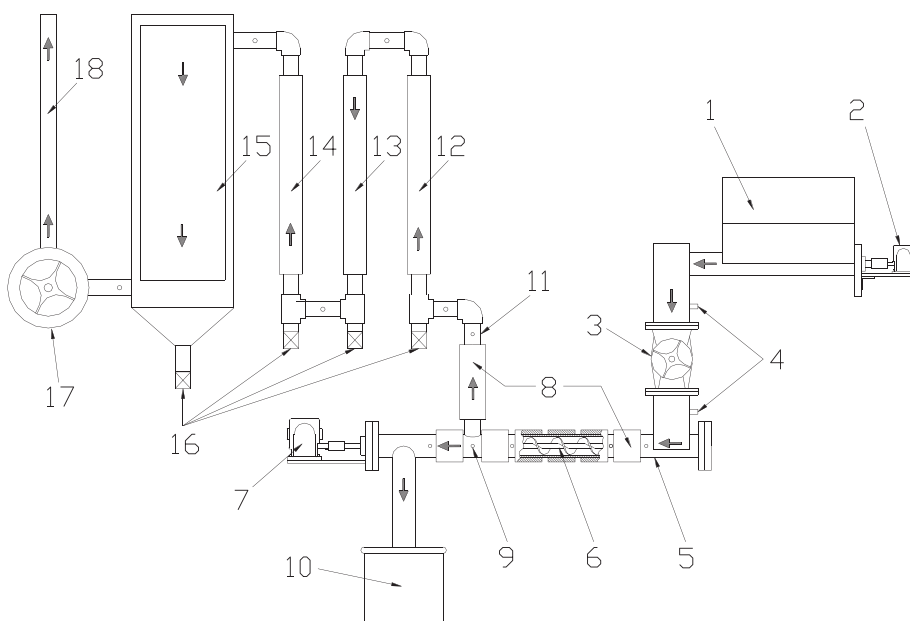
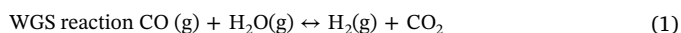


Fig. 1. Schematic of the pyrolysis reactor.

converting aldehydes and ketones to carboxylic acids, as well as oxidizing some of the phenols and alcohol. Tanneru and Steele [22] have successfully applied syngas to hydrotreat bio-oil and they pretreated bio-oils (water content in RB was about 29 vol%) in one stage during previous research. However, the hydrocracking of the first stage of products using syngas was not successful. Pure hydrogen was required to perform hydrocracking during a second stage treatment [22]. Moreover, 1st-stage hydrotreating with syngas followed by 2nd-stage hydrocracking with pure hydrogen was successful in producing pure hydrocarbons from RB, oxidized raw bio-oil (ORB), fractionated bio-oil (FB) and oxidized fractionated bio-oil (OFB) [23,24].

Tanneru et al. [22] and Wijayapala et al. [25] have proven that large amounts of water in bio-oil reacted with CO to produce H<sub>2</sub> and CO<sub>2</sub> in the presence of Cu-based WGS catalysts. H<sub>2</sub> already contained in the syngas combined with the H<sub>2</sub> produced by the WGS reaction was found to perform the hydrotreating reaction seen in Eq. (1).



Tanneru and Steele [22] applied pressurized (800 psi) synthesis gas produced from downdraft gasification comprised of 19% H<sub>2</sub>, 21% CO, 11% CO<sub>2</sub>, 2% CH<sub>4</sub> and 47% N<sub>2</sub>, on a moisture free basis, to perform syngas hydrotreating (HT-S) of ORB at 360 °C. About 95% of the H<sub>2</sub> and the entire CO volume were consumed during the syngas hydrotreating process. The resultant OLP properties were greatly improved in terms of hydrocarbons (HCs) proportions, oxygen content, total acid number (TAN) and viscosity.

By contrast to the H<sub>2</sub> content of 19% produced by the downdraft gasifier [26], a fluidized bed gasifier produced gas comprised of 39.6% H<sub>2</sub>, 43.4% CO, 0.3% CH<sub>4</sub>, 0.5% CO<sub>2</sub>, and 15.4% N<sub>2</sub>, on a moisture free basis. To determine the feasibility of applying the syngas [26], a model syngas mixture simulating the H<sub>2</sub> and CO components of 40 parts H<sub>2</sub> and 60 parts CO was applied for the application of hydrotreating the bio-oil with syngas by Luo et al. [24]. This experiment yielded 39.4 wt % OLP with 40% of the organic product being composed of HCs. The OLP had an oxygen content 13.9 wt%, TAN value of 44.7 mg KOH/g, and viscosity value of 117.8 cSt. The oxygen content, TAN and viscosity values in the produced OLP were much lower than the values found in the original bio-oil.

We hypothesize that a higher HT-S temperature of 400 °C may produce a higher quality OLP suitable for further applications. If successful, the upgrading of bio-oil by HT-S of OFB at distributed sites should be economically viable. The capital cost for syngas produced by

fluidized bed gasification is much less expensive than the capital cost for hydrogen production. The objective of the current research was to produce OLP by single stage syngas hydrotreating of OFB at 400 °C to obtain better yields with more HCs, a lower TAN value, a lower viscosity and lower oxygen content for further application.

## 2. Materials and methods

### 2.1. Catalyst and chemicals

Nickel/silica-alumina catalyst (~65 wt% nickel, ~10 wt% silica, 10 wt% alumina, and powder, with a surface area of 190 m<sup>2</sup>/g), oxidized copper, and potassium carbonate were purchased from Alfa Aesar. Syngas (H<sub>2</sub>/CO molar ratio of 4:6) and helium (He) gases were supplied by NexAir Gas Company. Hydrogen peroxide (30 wt% solution in water, certified ACS 30.0 to 32.0%), isopropanol (99.9%, HPLC Grade), dichloromethane (Stabilized/certified ACS), methanol (Stabilized/certified ACS) and oxone were purchased from Fisher Scientific. All catalysts and chemicals were used without further purification.

### 2.2. Fractionated and raw bio-oil production

Loblolly pine (*Pinus taeda*) was ground and sieved into a particle size range of 0.5–4 mm, and then oven-dried to a moisture content below 5 wt%. The fast pyrolysis reaction of the loblolly pine was conducted in a 7 kg/h auger-fed reactor at Mississippi State University (MSU). Fig. 1 shows the schematic of the MSU pyrolysis reactor.

The pyrolysis operation began with loblolly pine biomass particles poured into a feed hopper (1) and transferred via a motorized auger (2) to a rotary airlock valve (3). A nitrogen purge (4) of 1 scfm was introduced above and below the rotary airlock valve. Along with the nitrogen purge (4), the rotary airlock valve (3) prevented oxygen from entering the pyrolysis reactor and pyrolysis vapors from exiting the pyrolysis reactor while feeding biomass into the reactor (3 in. in diameter and 45 in. in length). The speed of motorized auger (6) inside the pyrolysis reactor (5) was 10 rpm with an applied pyrolysis temperature of 450 °C. The calculated residence time for the feed in the high temperature zone was approximately 1–2 s. The heat for the pyrolysis reactions was provided by multiple heaters along the reactor pipe, including a preheating zone (300 °C), a pyrolysis zone (450 °C) and a post heating zone (300 °C). Ceramic band heaters (8) around the outside of

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