

Hydrocarbon Production via Biomass Pyrolysis and Hydrodeoxygenation

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ABSTRACT

Bio-oils produced from pyrolysis of biomass are chemically complex compounds. As fuels they have a number of negative properties such as high acidity, water content, variable viscosity and heating values about half that of diesel fuel. These negative properties are related to the oxygenated compounds contained in bio-oils that result in a 45% oxygen content. For production of a viable fuel the raw bio-oils must be upgraded. The bio-oil hydrotreating process has been approached by applying hydrogenation catalysts under heat and pressure. Researchers have reported application of a successful two-stage catalytic hydrodeoxygenation (HDO) process. We have recently developed a single-stage HDO catalysis. The upgraded bio-oil contains hydrocarbons very similar to petroleum fuels. Yields of the upgraded bio-oils are more than 72% by energy capture. Future research on the upgraded product will focus on distillation and introduction into petroleum refineries and investigating the potential for direct blending with current petroleum fuels.

Keywords: pyrolysis, hydrodeoxygenation, hydrocarbon, biomass

1 INTRODUCTION

Bio-oil is produced by flash pyrolysis of small biomass particles at 400 to 650 degrees C in the absence of oxygen. The yield of bio-oil is relatively high at 60-percent dry weight basis or higher depending on the production process. Bio-oil chemical properties vary with the feedstock but woody biomass typically produces a mixture of 30-percent water, 30-percent phenolics, 20-percent aldehydes and ketones, 15-percent alcohols and 10-percent miscellaneous compounds (Bridgewater et al. 1999).

As a fuel bio-oil has environmental advantages when compared to fossil fuels because combusted bio-oil produces half the NO_x and no SO_x when compared to petroleum fuels. As a fuel derived from a renewable resource bio-oil is considered to be CO₂ neutral. Bio-oil can be burned directly in engines and electricity has been produced by bio-oil fueled diesel engines and turbines have been specially modified to successfully burn bio-oil. However, some properties of bio-oil such as lower octane, acidity, immiscibility, viscosity change over time and a distinctive odor have prevented its commercial use to date

for other than pilot and demonstration projects. Investigators now agree that some upgrading step is required prior to utilization of bio-oil as a fuel (Bridgewater et al. 1999).

Bio-oil can contain up to 45 percent oxygen which is responsible for various negative properties described. Catalytic hydrotreatments of liquid bio-oils to reduce the oxygen content have been investigated with standard petroleum hydrogenating procedures and catalysts by using slightly modified, current petroleum-refining technologies and infrastructure. Fuel grade hydrocarbons may be produced depending on the extent of the hydrogen treatments. Raw bio-oils, due to the high oxygen contents, cannot be refined using the current petroleum refining processes. Commonly, the hydrogen treatment for reducing or eliminating oxygen to the extent of transforming bio-oils to a liquid hydrocarbon mixture with properties very similar to petroleum crude oil is called hydrodeoxygenation (HDO) treatment (Scholze 2002). HDO treatments of raw bio-oils can be carried out very similarly to the hydrodesulfurization process used in the petroleum refining industry to reduce the sulfur content of petroleum crude oil. Both hydrodesulfurization and HDO require catalysts combined with some level of heat and pressure. Researchers have hypothesized that only minor changes are required for the current hydrodesulfurization processes and infrastructure of the petroleum industry to be applied to the HDO of bio-oil. Likewise, HDO treated bio-oils can potentially be refined in existing petroleum refineries, again with only minor adjustments to the current petroleum industry refinery infrastructure (Bridgewater and Cottam 1992).

Catalytic HDO research has, to-date, been based on application of traditional petroleum catalysts. Moderate successes in applying these HDO catalysts on bio-oils have been attained. However, specialized catalysts for bio-oil application, as opposed to petroleum applications, have yet to be developed. The complex chemistry of bio-oils presents a special challenge compared to processing of crude petroleum oils that are mainly composed of hydrocarbons. A promising approach identified by Bridgewater (1992) is the identification of a modified zeolite which is more selective toward bio-oil components and desired products.

The reduction of oxygen content of bio-oil has been shown to be achieved by catalytic hydroprocessing. Elliot (2007) has performed an extensive recent review of the history of catalytic hydroprocessing research. Bio-oil upgrading via hydrotreatment involves reaction of the bio-

oil oxygen with hydrogen in the presence of a hydrotreating catalyst. This results in the formation of water and the resultant production of an aqueous fraction that phase separates from the treated bio-oil fraction.

The approximately 25 percent of water and other inhibitory compounds contained in crude bio-oils have been shown to foul the catalysts applied during the hydrogen treatment step. In addition, many catalysts produce a highly viscous product during hydrotreating resulting from the previously described propensity for bio-oils to polymerize rapidly when heated as is necessary for successful hydrotreating catalysis.

As Elliott (2007) describes in his review, researchers at Pacific Northwest National Laboratory (PNNL) began to pioneer a two-stage bio-oil hydrotreatment method beginning in the 1980s. This method generally involved catalytic hydrotreatment at temperatures below 300°C in a first stage. The product from the first-stage hydrotreatment was then hydrocracked to gasoline range hydrocarbons at higher temperatures, normally below 400°C.

Elliot (2007) has updated the early PNNL reports on this two-stage process in his excellent historical review of bio-oil hydroprocessing research. The two-stage process was combined into a single nonisothermal catalyst bed and tested in a bench-scale mode in both upflow and downflow configurations. Initial upflow tests were performed on liquefaction products rather than fast pyrolysis oils. In these initial tests 22 catalysts were screened for efficacy. From among these 22 screened catalysts the researchers selected for further testing only CoMo 0402/S, HT 400/S and Ni-1404 as the most promising hydrotreating catalysts.

Recent research on HDO of bio-oil with several catalysts was reported by Wildschut and Heeres (2008). Ru/Al₂O₃, Ru/C, Ru/TiO₂, Pd/C, Pt/C and sulfided NiMo/Al₂O₃ and CoMo/Al₂O₃ were screened for comparable efficacy. A mild first-stage hydrotreating step was not performed. Rather, hydrotreating was performed on the raw bio-oil at 350°C and 200 bar pressure for reaction times of 4 h. Best result was for Ru/C that provided a 60% yield of HDO bio-oil with oxygen content lowered to 6% (based on the weight of products to initial raw bio-oil weight).

Elliott (2008) recently disclosed successful use of palladium based powdered catalysts for HDO of bio-oil and has claimed all catalysts containing palladium for this purpose.

In this paper, we reported an experimental study for the hydrodeoxygenation of fast-pyrolysis bio-oil. A commercial nickel catalyst has been explored and the product properties of the resulting hydrotreated bio-oil have been determined.

2 PROCEDURES

We performed mild hydrotreating tests with a commercial nickel catalyst. Our literature search found no application of this catalyst to hydrogenation of fast-

pyrolysis oils. Our preliminary research with this catalyst investigated temperatures between 300 to 400°C at 7 to 15 MPa of hydrogen pressure. Hydrotreating experiments were performed in a high-pressure autoclave in batch mode. Experiments with reaction time for stabilization purpose indicated that less than 30 minutes were required to reduce oxygen content in raw bio-oil from 45 to about 18.5% oxygen content in the upgraded product. No coking occurred and the catalyst was easily regenerated. Hydrotreating for 30 minutes followed by catalyst regeneration was performed 3 times with no observable influence on yield or catalyst quality.

Table 1. Catalytic operating conditions applied during hydrotreating of raw bio-oil.

| Operating condition | Value |
|-------------------------------------|-------|
| H ₂ consumption, L/L oil | 58 |
| LHSV | 0.80 |

3 RESULTS

The hydrogenated product from the catalytic hydrotreating at 2 h is lighter than water with a density of 0.85 g/ml and floated on the approximately 36% of water produced by the reaction. By weight, the total yield of the water and hydrogenated bio-oil was 85%. The hydrogenated product comprised 49 percentage points; solids residue lower than 11 percentage points contributed to the total yield with the remainder of the mass balance released as gas from the reactor. The residue is presumed to consist of uncatalyzed carbon. This residue rests at the bottom of the collection vessel below the water layer. The water layer is very distinct from the hydrogenated product and is easily separated with a separating funnel. Table 1 gives the catalytic operating conditions applied during hydrotreating. During catalysis hydrogen consumption was 58 liter per liter of oil (L/L oil) hydrotreated. LHSV was 0.80 h⁻¹.

Table 2. Properties of hydrotreated product following separation of aqueous fraction.

| Property | 30 min hydrotreating |
|--------------------------|----------------------|
| Oxygen content (%) | 18.5 |
| Hydrogen content (%) | 9.0 |
| Carbon content (%) | 72.2 |
| Viscosity (cSt) at 40 °C | 26 |
| Density (g/ml) | 1.15 |
| pH | 6.4 |
| TAN (mg) | 35.8 |

| | |
|-------------------|-----|
| KOH(g) | |
| Water content (%) | 5.1 |

The properties of the stabilized product are given in Table 2. Oxygen content was 18.5%, hydrogen content was 9.0% and carbon content was 72.2%. Water content in the separated hydrogenated product was 5.1%. Total acid number (TAN) prior to further deacidification was 35.8, a reduction of 62% from the 94 TAN value of the raw bio-oil. Viscosity of raw bio-oil was 40 while the hydrotreated bio-oil had a slightly reduced viscosity of 26.

Table 3. Viscosity change over time comparing raw and neutralized (TAN<5) hydrotreated bio-oils heated at 90°C for 0, 8 and 24 h (measured by Brookfield viscometer at 40°C).

| Time (h) | Raw bio-oil | Hydrotreated bio-oil |
|---|-------------|----------------------|
| t0 | 18 | 26 |
| t0 + 8 hours 8 hours storage at 90°C | 23 | 27 |
| t0 + 24 hours 24 hours storage at 90°C | 35 | 30 |
| Viscosity Increase (cSt/day) | 17 | 4 |

Aging studies were performed to test the stability of the mild hydrotreated bio-oil with respect to accelerated thermal aging. Viscosity was compared between raw and hydrotreated bio-oil. The two bio-oils were heated at 90°C for 0, 8 and 24 h. Results are given in Table 3 and show that, at t=0 h, hydrotreated bio-oil had a viscosity of 26 cSt which was 44% higher than the raw bio-oil value. This can be explained by mild polymerization reactions that occur with change of bio-oil pH during the HDO step. This is not an unusual finding. At t=8 h viscosity of raw bio-oil had risen to 23 cSt and after 24 h had increased to 35 cSt. Respective viscosity increase for the hydrotreated bio-oil was to 27 after 8 h and to 30 after 24 h. Therefore, the cSt value of viscosity increase for hydrotreated bio-oil was 4, comparing with that of raw bio-oil (17 cSt). It was nearly doubled after the 24 hours of aging at 90°C, which shows the hydrotreated bio-oil is more stable than raw bio-oil.

Simulated distillation (Figure 1) was performed to compare the properties of our hydrotreated bio-oil as to petroleum fuels (diesel and gasoline). As indicated in the figure the properties of our hydrotreated bio-oil closer to gasoline than diesel.

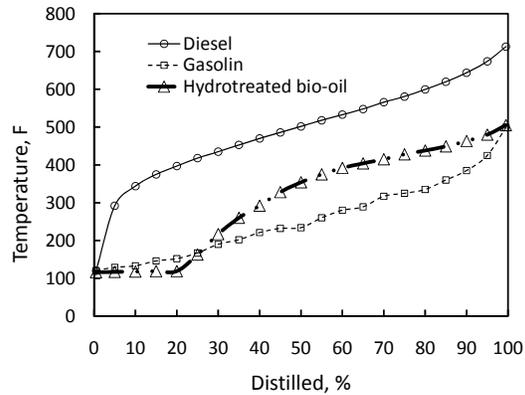


Figure 1. Simulated distillation GC of hydrotreated bio-oil, diesel and gasoline.

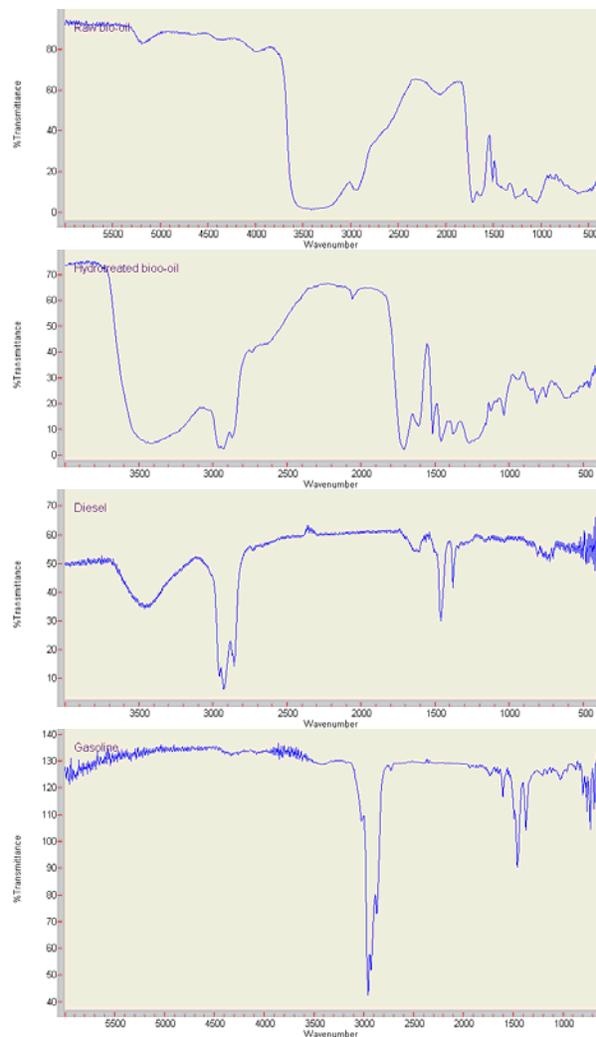


Figure 2. FTIR spectrums of raw bio-oil, hydrotreated bio-oil, diesel and gasoline.

FTIR results (Figure 2) of hydrotreated bio-oil in comparison with raw bio-oil and petroleum fuels (diesel and gasoline). As indicated in Figure 2 the hydrotreated bio-oil has relatively similar aromatic and alkane groups compared to these petroleum fuels.

We performed informal miscibility tests by blending our upgraded bio-oil with both petroleum diesel and gasoline fuels. Miscibility was complete with no settling out of the upgraded bio-oil over time.

4 CONCLUSIONS

Based on fast pyrolysis and hydrodeoxygenation testing, commercial nickel catalyst provides an effective hydrotreating process to accomplish oxygen removal from raw bio-oil. Carbon capture was high at 72%. Physical and chemical properties of the hydrodeoxygenated bio-oil indicated high stability and properties similar to both gasoline and diesel petroleum fuels. Miscibility tests indicated long term stability of the hydrodeoxygenated bio-oils when blended with both petroleum gasoline and diesel fuels.

REFERENCES

- [1] Bridgewater, A., C. Czernik, J. Diebold, D. Mekar and P. Radlein. "Fast Pyrolysis of Biomass: A Handbook." CPL Scientific Publishing Services, Ltd. Newbury, UK. 188p. 1999.
- [2] Bridgewater, A. V. and M. L. Cottam "Opportunities for biomass pyrolysis liquids production and upgrading." *Energy & Fuels* **6**(2): 113-120. 1992.
- [3] Elliott, D.C. "Historical developments in hydroprocessing bio-oils." *Energy and Fuels*, **21**, 1792-1817. 2007.
- [4] Elliott, D.C., J. Hu, T.R. Hart, G.G. Neuenschwander. "Palladium catalyzed hydrogenation of bio-oils and organic compounds." US Patent 7,425,657. 2008.
- [5] Wildschut, J. and H.J. Heeres. "Experimental studies on the upgrading of fast pyrolysis oil to liquid transportation fuels." In *Fuel Chemistry Division Preprints of the 235th American Chemical Society National Meeting and Exposition*. 53(1), 349. April 6-10, New Orleans, LA. 2008.