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Stabilization of bio-oils using low temperature, low pressure hydrogenation

Marjorie R. Rover [a], Patrick H. Hall [a], Patrick A. Johnston [a], Ryan G. Smith [a], Robert C. Brown [a,b,*]

[a] Bioeconomy Institute, Iowa State University, Ames, IA 50011, USA
[b] Department of Mechanical Engineering, Iowa State University, Ames, IA 50011, USA

HIGHLIGHTS

- Low-temperature, low-pressure hydrogenation of phenolic oils was investigated.
- Carbonyl groups were converted to alcohols and vinyl groups were saturated.
- Mass yields were 85–99.7% with virtually no coking.
- Viscosities of phenolic oils dropped several fold upon hydrogenation.
- Improves prospects for hydroprocessing phenolic oils to hydrocarbons.

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ABSTRACT

The superficial similarities between petroleum and bio-oil have encouraged efforts to employ petroleum hydroprocessing in the upgrading of bio-oil. Any facile comparison is overshadowed by the fact that petroleum consists of non-polar hydrocarbons that are relatively stable, requiring elevated temperatures and pressures to encourage chemical transformations, whereas bio-oil consists of oxygenated organic compounds whose high degree of functionality makes them chemically reactive even at low temperatures and pressures. Lignin-derived phenolic compounds readily polymerize and dehydrate to coke when hydroprocessed, resulting in low carbon yields of fuel range molecules and catalyst deactivation. In light of the limitations of conventional hydroprocessing, we explore low-temperature, low-pressure (LTLP) hydrogenation of pyrolysis-derived phenolics over 10% palladium on activated carbon (Pd/C) at 21 °C and 1 bar pressure as a way to produce stabilized bio-oil at high yields.

1. Introduction

Bio-oil is a liquid produced from the thermal deconstruction of biomass that superficially resembles petroleum. Both are dark, viscous liquids consisting of hundreds of organic compounds [1]. This similarity has encouraged attempts to hydroprocess bio-oil in a manner similar to that employed for petroleum, which has not been altogether successful. Such a facile comparison is overshadowed by the striking differences between the two substances. Petroleum consists of non-polar hydrocarbons that are relatively stable, requiring elevated temperatures and pressures (400–800 °C and 68–138 bar) [2] to encourage chemical transformations, whereas bio-oil consists of oxygenated organic compounds with high degrees of functionality that make them chemically reactive even at low temperatures and pressures.

The liquid product of fast pyrolysis, widely known as bio-oil, is an emulsion of predominantly lignin-derived phenolic oligomers in an aqueous phase containing primarily carbohydrate-derived compounds [3]. Bio-oil has several characteristics that make it undesirable as fuel [4] including poor storage stability [5], high acidity and corrosivity [5,6], low heating value, high viscosity, incomplete volatility [5], and immiscibility with petroleum fuels [3,7]. The key problem with upgrading bio-oil is its poor thermal stability at elevated temperatures, leading to heavy tar and coke formation, which rapidly deactivates upgrading catalysts [8–10]. Even when stored for long periods or heated in the absence of catalysts,

Abbreviations: LTLP, low-temperature low-pressure; DMSO, dimethyl sulfoxide; GPC, gel permeation chromatography; THF, tetrahydrofuran; CS, cornstover; RO, red oak.

* Corresponding author at: Iowa State University, Bioeconomy Institute, Department of Mechanical Engineering, 1140E BRL Bldg., Ames, IA 50011, USA. Tel.: +1 515 294 7934.
E-mail address: rcbrown3@iastate.edu (R.C. Brown).

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bio-oil tends to polymerize [11]. Unfortunately, these polymerization/condensation reactions are accelerated by the elevated temperatures typically employed in hydroprocessing [8] making severe hydroprocessing of raw bio-oil counterproductive to achieving high carbon yields of fuel-range molecules.

Recognizing that the high reactivity of bio-oil is a barrier to upgrading, researchers have attempted to stabilize bio-oil at milder hydroprocessing conditions. Baker and Elliott [12] reduced hydroprocessing temperature to around 250–270 °C from approximately 400 °C to prevent coking at 140 bar in the presence of cobalt and molybdenum (CoMo) catalyst. Although hydrogenation occurred with a conversion of 69 vol%, the loss of water and the saturation of carbon bonds increased the viscosity of the bio-oil from 10 cP to 14,200 cP at 60 °C [12]. Pacific Northwest National Laboratories also devised a three-stage process for hydrotreating bio-oil [13]. The first two stages, characterized as hydrotreating at 240 °C, 170 bar and 370 °C, 137 bar, respectively, were intended to partially deoxygenate and stabilize the bio-oil followed by more severe hydrocracking/hydrodeoxygenation at 425 °C, 87 bar to produce fuel-range hydrocarbon molecules [13]. Although partially successful, carbon yields under these conditions was still relatively modest and rapid coking of catalysts was still a problem.

Chaiwat et al. [14] performed a series of mild hydroprocessing tests on bio-oil at 175–300 °C and 56–184 bar pressure from 70 to 1380 min. The products obtained consisted of oil phase, water phase, and heavy compounds. The oil phase collected consisted of 7.8–63.8 wt% while the aqueous phase ranged from 30.2 to 54.4 wt%. The heavy compounds were 2.2–23.7 wt% of the product [14]. It was not clear whether the heavy compounds were suitable for hydrocracking to fuel range molecules, but the yield of potentially upgradable compounds was unacceptably low for commercial application.

In light of the high reactivity of phenolic oligomers, we explore the possibility that even so-called mild hydroprocessing, as currently defined, is too severe for the reactive feedstocks derived from biomass. We propose low-temperature, low-pressure (LTLP) hydrogenation of phenolics derived from bio-oil with the goal of producing a stable, low viscosity product at high yields.

2. Material and methods

The phenolics used in these experiments was produced by the fast pyrolysis of cornstover and red oak. As-received biomass was passed through a 60 hp hammer mill equipped with a 3 mm screen; resulting in a particle range of approximately 200 μm–3 mm.

Fast pyrolysis was performed in a fluidized bed reactor with a staged bio-oil recovery system [15]. Stage 1, a condenser, collects high boiling point compounds (i.e. anhydrosugars and phenolic oligomers) in the vapor phase according to dew point temperatures with the temperature controlled utilizing a shell-and-tube heat exchanger operated with gas inlet and outlet temperatures of 345 °C and 102 °C, respectively. Stage 2 is an electrostatic precipitator that collects aerosols formed during pyrolysis or during cooling in stage 1. It is operated at 40 kV DC and heat traced to 129 °C to prevent premature vapor condensation [15]. The five stages of bio-oil recovery are used with the purpose of separately collecting both the vapors and aerosols of the oligomer-rich phenolics and sugars in stages 1 and 2, a middle cut of monomeric phenols and furans in stages 3 and 4 and an aqueous phase that contains the large majority of "light oxygenates" in stage 5. Stages 1 and 2 is approximately 40–45 wt% of the produced bio-oil and account for 65–75% of the carbon in bio-oil. The middle cut, stages 3 and 4 are 10 wt% of the produced bio-oil while stage 5 is 45–50 wt% of the produced bio-oil [16]. Given that 65–75% of the carbon in bio-oil is collected in stages 1 and 2, it is important to establish the commercial importance of stabilization and utilization of upgrading techniques for both fuel and chemical applications. Complete details of the reactor design and collection system are found in Pollard et al. [16] and Rover et al. [15]. The phenolics used in these experiments were recovered in stages 1 and 2 and collected in fractions 1 and 2. Although all fractions might benefit from improved stabilization, the phenolic oils recovered from stages 1 and 2 are particularly susceptible to polymerization and viscosity thickening in storage and were selected for LTLP hydrogenation in this study. All experiments were performed at 21 °C and 1 bar (absolute) pressure.

A water wash was used to separate the water soluble sugars from the water insoluble phenolics utilizing a 1:1 ratio of deionized water to fractions 1 and 2 bio-oil. The resulting solution was stirred, placed on a shaker table (MaxQ 2506, Thermo Scientific, Hanover Park, IL) for 30 m at 250 motions min^{-1} and centrifuged (accuSpin 1R, Thermo Scientific, Hanover Park, IL) at 2561 g force for 30 min. The water soluble portion (sugar-rich solution) was decanted [17].

The phenolics prepared from cornstover (CS) bio-oil were produced and stored at 5 °C for six months prior to hydrogenation. The phenolics prepared from red oak (RO) were immediately hydrogenated after their production. This difference in the time of preparation was not originally thought to be important although, as subsequently described, there was some evidence that the stored corn stover sample oligomerized (aged) even in cold storage.

Sample size for the hydrogenation was approximately 100 g of both cornstover fractions 1 and 2 phenolics, which were placed separately in a 1000 mL round bottom flask along with a large stir bar. Fraction 1 was dissolved in 300 mL methanol and fraction 2 was dissolved in 500 mL methanol. Sample size for red oak fractions 1 and 2 phenolics was 40 g dissolved in 200 mL and 300 mL methanol, respectively. The flask was placed under vacuum 3 times to remove any oxygen present and then purged each time with argon. The catalyst (1.5 g for cornstover and 0.5 g for red oak), 10% Pd/C, was quickly added to the round bottom flask. Higher catalyst loading was utilized for the cornstover samples in order to achieve favorable results, whereas, lower catalyst loading was sufficient for the red oak phenolic oils. The Pd/C catalyst used for hydrogenation of the phenolics was chosen for its high activity at mild processing conditions [18] and the ability to recover the Pd metal by simply burning off the carbon support [19–21]. The flask was again placed under vacuum and then a hydrogen atmosphere was introduced to the system. The flask was stirred at 750 rpm with hydrogen flowing at 0.25 L min^{-1} through the 1000 mL round bottom flask and out the bubbler for 16 h in a fume hood. Upon completion of the hydrogenation, the samples were filtered with a fritted funnel using Celite® 503 and rinsed 3 times (100 mL, 50 mL, 50 mL) with methanol. The hydrogenated samples were rotary evaporated at 20 °C for 1.5 h to remove the methanol solvent.

Proton NMR was carried out using an Agilent/Varian MR-400 (Agilent Technologies, Inc., Santa Clara, CA) with a narrow bore 9.4 T/400 MHz magnet equipped with OneNMR pulse-field-gradient probe. VNMRJ 3.0 was used for data acquisition with the MNova software (MestReNova, Escondido, CA) for data processing. Fourier transformed spectra were auto-phased and baseline corrected with dimethyl sulfoxide-d_6 (DMSO-d_6) solvent referenced at 2.50 ppm. Integration of the DMSO was normalized to 1.00. Subsequent integration of the various spectral regions (δ 10–8.0, 8.0–6.8, 6.4–4.2, 4.2–3.0, 2.2–1.6, and 1.6–0.0 ppm) was performed. DMSO and residual methanol solvent peaks were