Hydrodeoxygenation of fast-pyrolysis bio-oils from various feedstocks using carbon-supported catalysts ☆

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ABSTRACT

In this paper, we sought to elucidate the relationships between biomass feedstock type and the suitability of their fast-pyrolysis bio-oils for hydrodeoxygenation (HDO) upgrading. Switchgrass, *Eucalyptus benthamii*, and equine manure feedstocks were pyrolyzed into bio-oil using a continuous fast-pyrolysis system. We also synthesized variations of switchgrass bio-oil using catalytic pyrolysis methods (HZSM-5 catalyst or tail-gas recycle method). Bio-oil samples underwent batch HDO reactions at 320 °C under ~2100 psi H_2 atmosphere for 4 h, using Pt, Ru, or Pd on carbon supports. Hydrogen consumption was measured and correlated with compositional trends. The resulting organic, aqueous, and gas phases were analyzed for their chemical compositions. Mass balances indicate little coke formation. Switchgrass bio-oil over Pt/C performed the best in terms of hydrogen consumption efficiency, deoxygenation efficiency, and types of upgraded bio-oil compounds. Eucalyptus feedstocks consistently consumed more than twice the normal amount of hydrogen gas per run, primarily due to the elevated syringol content. Catalytically pyrolyzed bio-oils deoxygenated poorly over Pt/C but hydrogenated more extensively than other oils. Although the relative deoxygenation ($\%DO_{rel}$) varied based on feedstock and catalyst, the absolute deoxygenation ($\%DO_{abs}$) depended only on the overall yield. The total extent of upgrading (hydrogenation + deoxygenation) remained independent of feedstock and catalyst.

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1. Introduction

As the global rate of energy consumption increases, the need for sustainable renewable fuels escalates. The global supply of fossil fuels cannot meet the demand that is set by developing countries [1]. Hence, alternative and efficient energy sources are needed to mitigate the shortage. Although energy sources such as wind and solar are environmentally friendly, they still are impractical for many user applications; they also cannot replace the abundance of commodity chemicals and high-demand coproducts that emanate from fossil fuels. Furthermore, while corn grain ethanol has proven to be an effective alternative fuel [2], the U.S. Energy Independence and Security Act (EISA) sets a restriction on the maximum corn starch-based fuel obtained by the year 2022. Of all the methods investigated, thermochemical conversion of biomass shows the most promise for scalability, efficiency, reduction of greenhouse gases, and production of coproducts. Methods such as liquefaction [3,4], pyrolysis [5,2], and gasification [6] all fall under this category.

In particular, fast pyrolysis of biomass is highly effective at breaking down macromolecular structures into smaller organic compounds, the mixture of which has an appearance resembling liquid crude oil (i.e. "bio-oil"). Pyrolysis is one of the very few processes that is inherently carbon-negative [7], if all of its products are utilized to their advantage. Depending on the biomass feedstock used, fast pyrolysis bio-oil composition can drastically vary. Woody [8] and proteinaceous [9] biomasses, grasses [10], and animal waste [11] have been pyrolyzed into crude bio-oil. This apparent process neutrality with regard to feedstock makes fast pyrolysis easily translatable to a wide variety of agricultural climates and economies. Bio-oils from lignocellulosic biomasses yield highly aromatic mixtures, which carry greater potential for fuel efficiency. Due to the abundance of acid, high viscosity, and heteroatom contaminants, bio-oil must be catalytically upgraded and hydrotreated in order to serve as a fungible fuel. Hydrodeoxygenation (HDO) reactions are employed in order to increase the H:C and decrease the O:C atomistic ratios. Supported Ru, Pt, and Pd are catalysts which are commonly employed for this purpose. Elliot et. al. [12] demonstrated a two-stage continuous HDO configuration for the upgrading of pine bio-oil. Mercader and coworkers extracted the acids from bio-oil before HDO, to examine the efficacy on catalytic upgrading [13]. Several other studies show ruthenium catalysts to be effective for deoxygenation [14,15]. Despite the abundance of HDO studies [16], very few have gone beyond the upgrading of wood-based bio-oil [17]. Since feedstocks have a large effect on the bio-oil quality, so too they would affect the HDO efficacy. In

order for fast pyrolysis to become a viable fuel source, both the pyrolysis and upgrading steps should translate well to different feedstocks and hence, to different global economies. A thorough investigation is needed in order to elucidate the relationship between biomass feedstock and upgradability.

Also, certain process conditions affect the interactions of bio-oil components with the catalyst sites. For example, Subramanian and co-workers [18,19] proposed a shift in catalytic pathways by changing the reaction solvent for carbon-supported catalysts. The benefits of aqueous solvent effects have yet to be realized *in situ* for HDO of bio-oil, in contrast to model compounds. Catalytic pyrolysis processes also have a strong effect on the upgradability of bio-oil. Our goal was to elucidate the effect of various feedstocks and feedstock processing on HDO, both with regard to efficiency and quality of upgraded product. The biomasses we investigated cover a range of biomass types, under processing conditions that allow for greater contact between the bio-oil components and catalyst sites.

2. Materials and methods

2.1. Bio-oil production

All feedstocks were ground and dried prior to processing. Switchgrass feedstock was obtained from the McDonnell Farm (East Greenville, PA, USA), horse manure from the Equine Rehabilitation Center at Morrisville State College (Morrisville, NY, USA), and *Eucalyptus benthamii* from Embrapa Forestry (Candoi, Parana, Brazil). Feedstock fast-pyrolysis was carried out in the ERRC fluidized bed fast pyrolysis system, as described previously [10]. Briefly, 2 kg/h of feedstock is fed through a fluidized sand bed reactor under nitrogen at 500 °C. Catalytic pyrolysis was similarly carried out by replacing the sand bed with HZSM-5 catalyst (Zeolyst International, USA). The resulting vapors then pass through a cyclone which separates out solid char particles. Subsequently, liquid phases are condensed from the vapor by 4 condensers in series. Then the oil phase is precipitated from the non-condensable gases (NCGs) by two electrostatic precipitators (ESPs) in series. All experiments used the oil obtained from the ESPs. For recycle experiments [20], a fraction of the NCG stream was mixed with the N_2 stream and recycled into the fluidized bed, using a preheater and gas blower.

2.2. Hydrodeoxygenation

Batch hydrodeoxygenation reaction experiments were carried out in a Parr Series 4598 100 mL bench-top reactor. A Parr 4848B controller was used to monitor the vessel pressure and to control the internal temperature and impeller mixing speed. The reactor can withstand a maximum pressure of 5000 psi at 500 °C. Hydrogen was supplied from a reservoir tank via a pressure regulator. A constant pressure of hydrogen was delivered from the regulator to the reactor through a primary valve, which remained open for the duration of the experiment. Hydrogen consumption over time was measured by monitoring the reservoir pressure drop, while taking into account gas production from HDO reactions. To ensure adequate gas distribution, a dip-tube introduced hydrogen internally from the primary valve to the reactor vessel's bottom. The reactor was modified to accommodate a manifold apparatus for injecting liquid samples into the reactor through a secondary valve, all while the reactor is pressurized. Liquid flow through the manifold is controlled with a modified HPLC pump (Scientific Systems, Inc.), and the manifold piping was continuously warmed with heating tape.

All HDO catalysts (Johnson Matthey, Inc., UK) consisted of a powder charcoal support with 5% metal loading (Pt, Ru, or Pd). For all HDO experiments, 0.5 g catalyst and 40 mL deionized water were first loaded into the reactor vessel. The vessel was then clamped shut and flushed with hydrogen 3 times to displace air. After charging the vessel with 1100 psi hydrogen, the water/catalyst slurry was lightly stirred at 300 rpm while a furnace heated the vessel to an internal temperature

of 320 °C. The hydrogen reservoir pressure regulator was then increased to 2100 psi. After providing sufficient time for catalyst reduction, ~9 g of bio-oil was injected into the reactor, and the mixer speed was increased to 1200 rpm. After 4 h, the primary hydrogen valve was closed off, the heater was removed, and the mixer speed was decreased to 300 rpm. After gradually cooling the reactor and halting the mixer, non-condensable gases were vented into a collection bag and further analyzed. The aqueous phase was decanted from the vessel and centrifuged to remove any partially miscible components. The vessel and the reactor parts were washed with acetone to collect any accumulated oil. The acetone washings were filtered through a 0.45 μm PTFE filter to remove the catalyst, and the acetone was removed by rotary evaporation. Experiments were performed in duplicate.

2.3. Characterization

Elemental analysis (CHNS) was conducted via a Thermo EA1112 CHNS analyzer. Oxygen content was calculated by difference, and water content was subtracted. Moisture content was measured with Karl-Fischer titration in methanol with Hydranal Karl-Fischer Composite 5 (Fluka) as the titrant. Total acid number (TAN) was measured using a Mettler T70 autotitrator using 0.1 M KOH in isopropanol as the titrant and wet ethanol as the titration solvent. Gas chromatography with mass spectroscopy (GC–MS) analysis of liquid products was performed on a Shimadzu GCMS QC-2010. The column used was a DB-1701, 60 m × 0.25 mm, 0.25 μm film thickness. The oven temperature was programmed to hold at 45 °C for 4 min, ramp at 3 °C/min to 280 °C and hold at 280 °C for 20 min. The injector temperature was 250 °C, and the injector split ratio set to 30:1. Helium carrier gas flowed at 1 mL/min. GC–MS analysis of gaseous products was performed on an Agilent 6890N gas chromatograph equipped with an Agilent 5973 mass selective detector. Analyses were performed with a fused silica capillary column, CP-PoraBOND Q, 25 m × 0.25 mm (Varian, Palo Alto, CA). The programmed method held the temperature at 35 °C for 3 min, then increased to 150 °C at 5 °C/min, then increased to 250 °C at 10 °C/min. The final temperature was held for 30 min. Gas concentrations were calculated relative to calibration curves of a gas mixture standard: CO, CH_4, CO_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8, and C_4H_{10} mixed in helium (Scott Specialty Gases, Plumsteadville, PA).

3. Results and discussion

3.1. Bio-oil composition

The experimental study was restricted to three types of biomass feedstock. We examined switchgrass ("SwG"), *E. benthamii*, ("Eucal") and equine manure ("Manu") as representatives of herbaceous grasses, woody biomass, and animal waste, respectively. These particular feedstocks were selected for their abundance, importance to U.S. agriculture, and fundamental differences in feedstock characteristics. Alongside normal switchgrass bio-oil, two variations in partially deoxygenated switchgrass bio-oil were produced: 1) switchgrass catalytically pyrolyzed with HZSM-5 *in situ* ("cat-SwG") and 2) switchgrass pyrolyzed under an atmosphere produced by recycling the exhaust gas into the pyrolysis fluidized bed ("SwG-rec"). For HDO reactions, a moderate catalyst loading ratio was used in order to eliminate effects of catalyst overloading, such as excessive coking or cracking. Using water as a solvent for carbon-supported catalysts produces three beneficial effects: 1) highly acidic and other low-value oxygenated components transfer to the aqueous phase 2) beneficial components which are partially miscible in water are not excluded from HDO and 3) for particularly strong catalysts, water regulates the catalyst site interactions with bio-oil components [19]. Although some higher activation energies are satisfied by higher reaction temperatures (>320 °C), a consequently higher system pressure is necessary in order that water remains as a compressed liquid. Hence, one limitation of using water as a solvent is that higher