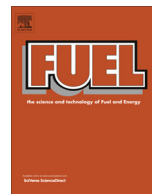


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Hydrotreating of fast pyrolysis oils from protein-rich pennycress seed presscake [☆]

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HIGHLIGHTS

- Oil seed presscakes are a source of proteinaceous biomass.
- Stable pyrolysis oils are produced from pennycress presscake.
- Hydrotreating over Ru/C and Pd/C reduced oxygen content of bio-oils.
- Upgraded products were characterized by GC × GC and NMR.
- Upgraded bio-oil from presscake contained fewer heteroatoms than that from wood.

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ABSTRACT

The fast pyrolysis oils produced from proteinaceous biomass, such as pennycress presscake differ significantly from those produced from biomass with mostly lignocellulosic composition. Those from proteinaceous biomass tend to be deoxygenated, contain more nitrogen, be less acidic and be more stable. Because their composition is different, their behavior in and products from upgrading via hydrotreating will be different. We studied the mild batch hydrogenation of the pyrolysis oil produced from pennycress presscake at ~13.8 MPa (138 bar) H₂ and 320 °C over five precious metal on charcoal catalysts: two Ru/C catalysts, two Pd/C catalysts, and one Pt/C catalyst. The liquid products were characterized by elemental analysis, GC × GC/MS and NMR. The Ru catalysts were most effective at further deoxygenating the pyrolysis oils, with the Pd catalyst slightly less effective, and the Pt catalyst the least effective. None of the catalysts were highly effective for hydrogenation, though among them Pt removed the most nitrogen from the liquids. Using the best catalysts, an upgraded pyrolysis oil containing <15 wt% total heteroatom content (O + N + S) with an HHV of 37.0 MJ/mg was realized. Compared with wood pyrolysis oils upgraded at similar conditions, the upgraded pyrolysis oils from pennycress presscake had lower oxygen and total heteroatom (O, N, and S) content, had higher energy content and were closer compositionally to petroleum. The products were very rich in long aliphatic hydrocarbon chains; these large aliphatic moieties were present in both purely hydrocarbon compounds and in heteroatom containing compounds especially alkyl amides.

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1. Introduction

Fast pyrolysis is a facile method for producing high yields of renewable liquid fuel intermediates from biomass. These pyrolysis oils can be upgraded to hydrocarbon fuels; the most effective upgrading processes usually involve catalytic hydrotreating. Most attention and research in this area is applied to conversion of bio-

mass of a highly lignocellulosic nature including wood, herbaceous energy crops (e.g. switchgrass) and agricultural residues (e.g. corn stover, straws). However, there are other potential biomass feedstocks whose composition differs greatly from these. One category of such feedstocks is proteinaceous biomass, which contains significantly more nitrogen than do most lignocellulosic feedstocks. Examples of potential proteinaceous biomass feedstocks include oil seed presscakes (meals), manures, legume residues, and aquatic species such as algae. Several examples of production of bio-oil from such materials via pyrolysis methods have been reported [1–7], but often they are treated in discussions as though they are the same as other lignocellulosic biomass. We have recently reported on the important differences in the pyrolysis behavior and

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the properties and composition of bio-oil derived from proteinaceous biomass including the deoxygenation effect the presence of nucleophilic nitrogen has during the pyrolysis process [8,9]. As a result of the higher concentration of nitrogen and lower concentration of oxygen, pyrolysis oils derived from proteinaceous biomass tend to be less acidic, more stable, and have higher energy content than those from most lignocellulosic biomass. This is largely due to the substitution of oxygen by nitrogen during pyrolysis via reactions of nucleophilic organonitrogen compounds with electrophilic oxygenated compounds. However, the properties of these bio-oils can still be improved by hydrotreating to reduce heteroatom content (O, N, and S) and to make them more useful as direct fuels, refinery blend stocks, fuels, or chemicals feedstock.

Hydrodeoxygenation (HDO) of pyrolysis oils of mostly lignocellulosic biomass has been extensively studied, and has been reviewed by both Furimsky [10] and Elliott [11]. Elliott has also demonstrated an effective two stage process for HDO of pyrolysis oils of wood and corn stover [12], utilizing first a relatively mild hydrotreating process utilizing a Pd on C catalysts followed by more severe hydrocracking over traditionally hydrodesulfurization (HDS) catalysts such as cobalt–molybdenum (CoMo) and nickel–molybdenum sulfides. Wildschut et al. have also extensively studied the hydrotreating of wood pyrolysis oils over Pd, Pt, and Ru catalysts [13,14]. However, there has been little attention paid to the upgrading strategies for pyrolysis oil from proteinaceous biomass. The closest example is a recent report that studied the hydronitrogenation (HDN) of highly solvent diluted pyrolysis oils of sewage sludge over sulfide CoMo catalyst [15]. Because the composition of pyrolysis liquids from proteinaceous biomass differs greatly from that produced from wood or grasses, their behavior in catalytic hydrogenation reactions will be significantly different. Given the favorable properties that the pyrolysis oil fuel intermediates from proteinaceous biomass “as produced” have already exhibited it would be interesting to compare their upgrading characteristics (hydrogen use, product distribution, etc.) to those from mostly lignocellulosic biomass. Therefore, we studied the mild slurry phase hydrogenation of the pyrolysis liquids of pennycress oil seed presscake utilizing Pd/C, Pt/C and Ru/C catalysts in a batch mode Parr reactor.

2. Methods and materials

2.1. Pyrolysis oil and catalysts

The pyrolysis oil used as starting material was produced from pennycress presscake using the ERRC fluidized bed fast pyrolysis system. The fraction of the pyrolysis oil collected via electrostatic precipitation (ESP) was used in these studies, due to its low water content (~7 wt%) and homogeneity. Details of the pyrolysis setup and reactions have been previously reported [8]. The precious metal on charcoal catalysts were supplied by Johnson Matthey, Inc. (UK).

2.2. Hydrogenation reactions

Hydrogenation reactions were performed in a 100 mL Parr Series 4593 bench top micro-reactor. The maximum pressure for this reactor is 20.7 MPa (207 bar), and the maximum temperature is 350 °C. The vessel was heat traced with Thermolyne flexible heating tape with temperature controlled by an OptiChem CG-15001 series (OptiChem, Vineland, NJ 08360) unit fitted with a CAL 3200 auto-tune (CAL Controls, Libertyville, IL 60048) temperature controller. The reactor vessel was fully insulated to help reach and maintain desired reaction temperatures. Reactions were performed on two different scales, one with ~400 mg of pyrolysis

oil and one with ~10 g of pyrolysis oil. In each case catalyst loading was 10% w/w.

For the smaller scale reactions the vessel was charged with five ½-dram vials each containing 400 mg of pyrolysis oil, 40 mg of catalyst and a small stirring bar and capped with a crimp top cap with a metal septum pierced with a needle to allow entry of hydrogen but minimize escape of liquid products. The vessel was then charged to 13.8 MPa (138 bar) and heated to 320 °C. After 5 h, the vessel was depressurized and the vials washed with 3 mL MeOH. The MeOH washings were filtered through a 0.45 µm PTFE filter and analyzed by GC × GC/MS. These reactions were repeated three times for GC × GC/MS comparative statistical analysis (see below).

For the larger scale reactions, the vessel was charged with approximately 10 g pyrolysis oil and 1 g of catalyst (5% metal loading on charcoal) and a 3 cm magnetic stir bar. The vessel was placed on a magnetic stir plate, pressurized with H₂ and flushed 6 times to displace air. The vessel was then charged to 12.8 MPa (127.6 bar) and heated to 320 °C. The reaction required a longer time at this scale, probably because of mass transfer issues between the hydrogen and pyrolysis oil/catalyst slurry. After 15 h, the reactor was depressurized with the gas collected in a gas bag for analysis. The vessel was then opened and the slurry removed via syringe. The reactor was then rinsed several times with acetone and the rinsing added to the removed slurry. The solution was then filtered and the filter cake was washed with acetone several times. After drying the solids yield was measured by difference of the filter cake and solid catalyst used. Acetone was removed *in vacuo* from the filtrate and the liquid yield determined gravimetrically. Hydrogen consumption was measured using the difference in pressure before and after the reaction and accounting for the production of product gases. Larger scale reactions were performed in duplicate.

Collected gas was analyzed on an Agilent 6890N gas chromatograph (GC) equipped with an Agilent 5973 mass selective detector. Analyses were performed using a fused silica capillary column, CP-PoraBOND Q, 25 m × 0.25 mm (Varian, Palo Alto, CA) with the following program: 3 min at 35 °C then ramped at 5 °C/min up to 150 °C followed by 10 °C/min up to 250 °C and held for 30 min. The concentration of gases were quantified with calibration curves produced using a standard gas mixture comprising CO, CO₂, CH₄, C₂H₄, C₂H₆, C₃H₆, C₃H₈, and C₄H₁₀ in helium (custom-mixed by Scott Specialty Gases, Plumsteadville, PA).

2.3. Product characterization

Elemental (CHNS) analysis was carried out using a Thermo EA1112 CHNS analyzer. Water content was measured using Karl-Fischer titration in methanol with Hydranal Karl-Fischer Composite 5 (Fluka) used as titrant. Oxygen content was determined by difference after measuring CHNS and water. Total acid number (TAN) was measured using a Mettler T70 automatic titrator using 0.1 M KOH in isopropanol as titrant and wet ethanol as the titration solvent. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a 400 MHz Varian Inova spectrometer in methanol-d₄ at 40 °C, as described by Mullen et al. [16]

The fifteen samples from the small scale reactions described above were analyzed by GC × GC/MS with a Shimadzu QC-2010 GC and QP-2010S MSD and a Zoex ZX-2 LN2 cooled-loop GC × GC thermal modulation system. Samples were 15 wt% in methanol. The first-dimension separation was performed on a 60 m Restek 1701 column (0.25 mm internal diameter and 0.25 µm film thickness) and the second-dimension separation used a 2 m Restek DB-1 column (0.25 mm and 0.25 µm film thickness). The flow rate was 3 mL/min He, with a 30:1 split ratio. The temperature program was 45 °C for 4 min, increased by 3 °C/min to 280 °C, then held for

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