



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 hydrodenitrogenation, 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

20 min. The total run time was 102 min including column cleanup, but data was acquired only from 9.5 to 70 min. The modulator cycle was 4 s. The mass spectrometer used 70 eV electron impact (EI) ionization and acquired data over the mass-to-charge (m/z) range 35–400.5, at a sampling rate of 20 spectra per second.

The GC \times GC/MS data was analyzed with GC Image GC \times GC Edition Software, Release 2.3a0. The analysis followed the process outlined by Reichenbach et al. [17] to comprehensively compare the fifteen chromatograms on the basis of aligned peak-region features [18]. The result is a matrix of values with rows for each chromatogram, columns for each of the peak-region features that comprehensively cover the peaks in the chromatograms, and values that indicate the detector response in each region relative to the detector responses in all regions of the chromatogram (i.e., the percent-responses). From that matrix, the following is computed.

- $\mu_{i,k}$ and $\sigma_{i,k}^2$: the means and variances for the percent-responses, respectively for catalyst i in region k .
- $D_{i,j,k} = (\mu_{i,k} - \mu_{j,k})$: the difference between the percent-response means for catalysts i and j in region k .
- $S_{i,j,k} = (\mu_{i,k} - \mu_{j,k})^2 / (\sigma_{i,k}^2 + \sigma_{j,k}^2)$: the Fisher's Discriminant Ratio of the percent-responses for catalysts i and j in region k .

The differences between the percent-response means reflect compositional differences between samples from different catalysts. The Fisher's Discriminant Ratio is used to confirm the statistical significance of the differences.

3. Results and discussion

The mass balance of the reactions for each catalyst is provided in Table 1. Yields were based on the sum of the masses of liquid input and H_2 consumed by the reaction. Hydrogen consumption was highest when the Pd-A catalyst was used, at 6.2 g/L of pyrolysis oil input. Reactions using Pd-B and both Ru catalysts consumed about 5 g of hydrogen per liter of pyrolysis oil. The Pt catalyst consumed the least amount of hydrogen at 3.9 g/L of pyrolysis oil input. Liquid product yields ranged from 67% to 85%. A small amount of solid was formed averaging 0.5–2%, except in the case of the reaction with the Pd-B catalyst where conversion to solid was 12%. Gas (CO , CO_2 , and C_1 – C_4 hydrocarbons) produced ranged from 2.1% to 5%. Overall mass balance was 75–90% closure. Potential sources of mass loss include heavy materials stuck to the stir bar, material that escaped into the gas feed line of the reactor, and highly volatile compounds that could have been lost during rotary evaporation of the acetone washes.

The elemental analysis of the liquid products from the hydrogenation of the pennycress presscake pyrolysis oil over the five catalysts studied is presented in Table 2. All of the catalysts were effective for removing the sulfur present in the starting materials (~ 0.5 wt%). For deoxygenation, the Ru and Pd catalysts were more effective than was the Pt catalyst. This is consistent with the results of Wildschut et al. [13] on studies of deoxygenation of beech wood pyrolysis oils with a similar set of catalyst and conditions and also

consistent with results using the same catalysts in the same reactor on white oak pyrolysis oils produced in our lab (Table 3). Ru-A was the only catalyst of the five screened to produce a completely biphasic product; this is partially a result of using low water content pyrolysis oils as starting materials. The products of the hydrogenation over Ru-B and both Pd catalysts were emulsions at room temperature and biphasic after refrigeration at 5 °C. The products from the Pt-catalyzed reaction were homogeneous. If more water was in the system to start, for example if whole pyrolysis liquids were used, more phase separation would likely have occurred. The top organic layer of that product from hydrogenation over the Ru-A catalyst had an oxygen content of 7.4% (dry basis) and a C/O ratio of 13.8, increasing from 6.1 in the raw pyrolysis oil. The Ru-B and both Pd catalysts produced completely homogenous liquids with oxygen contents of 9–10% and C/O ratios of about 10. The Pt catalyst was the least effective for the rejection of oxygen with the fraction of oxygen in the product actually slightly increasing from the starting material; made possible by the decrease in nitrogen content of the product.

Overall the catalytic hydrogenation over these catalysts was less effective at removing nitrogen than oxygen. The best catalyst for N removal was the Pt catalyst which rejected 34% of the nitrogen in the pyrolysis oil starting materials. Under Pt-catalyzed hydrogenation the nitrogen content of the liquid decreased from 8.5 wt% to 5.6 wt%, increasing the C/N ratio to 14.2 from 9.4 in the starting material. The Ru and Pd both removed smaller amounts of N than with both sets of catalysts increasing C/N ratios to between 13.0 and 13.7.

Taking the removal of a combination of S, O and N into account the trend for overall heteroatom removal was the same as for oxygen removal due to the general ineffectiveness of catalysts at removing N. Total heteroatom content removal was best achieved by the Ru catalysts, followed by the Pd catalysts, and the Pt catalyst was the least effective at overall heteroatom removal. The upgraded products were found to have much higher energy content than the pyrolysis oil starting material. Consistent with the trend in heteroatom removal the hydrotreatment over the Ru and Pd catalyst produced the products with the highest high heating values, up to 37.3 MJ/kg compared with 31.0 MJ/kg for the untreated pennycress presscake pyrolysis oil. All of the catalysts were also effective at further reducing the acidity of the pyrolysis oil. The total acid number (TAN) was reduced from 84 mg KOH/g in the pyrolysis oil starting material to <20 mg KOH/g for all of the hydrotreated products indicating that the hydrotreatment over all catalysts was effective at eliminating protic groups ($-(=O)OH$, $-OH$). This reduces the polarity of the liquids and increases their miscibility with hydrocarbons for use in fuels or refinery blendstocks.

Compared with pyrolysis oils from oak upgraded in the same system or from beech wood under similar conditions as reported from Wildschut et al. [13] the upgraded pyrolysis oils from pennycress presscake had a lower overall heteroatom content, and a higher H/C ratio. Fig. 1a and b are Van Krevlen type diagrams that compare the biomass and pyrolysis oils of pennycress presscake, wood, and the products upgraded by the methods reported here. Fig. 1a is a traditional Van Krevlen diagram that only accounts for O/C and H/C ratios and Fig. 1b is a modified diagram that also considers S and N content on the horizontal axis. These figures demonstrate the advantage of using proteinaceous biomass such as pennycress presscake for fast pyrolysis, even when its high nitrogen content is considered. In addition to the high energy content, and better stability of the fast pyrolysis liquids [8,9], this work demonstrates that after the same upgrading process a material closer to the elemental composition of petroleum is produced from the pyrolysis oils of pennycress presscake than from those of wood. However, before these upgraded pyrolysis oils are used as fuel, the

Table 1
Mass balances (wt%) for hydrogenation of pennycress presscake pyrolysis oils.

	Pd/C A	Pd/C B	Pt/C	Ru/C A	Ru/C B
H_2 consumed (g/L py-oil)	6.17	5.01	4.64	5.00	4.32
Liquid	72.5	68.3	67.1	72.6	81.0
Gas	5.3	2.2	2.1	2.8	4.0
Solid	2.3	12.2	2.4	1.9	0.4
Closure	80.1	82.7	71.6	77.3	85.4

Table 2
Elemental analysis of hydrogenated pennycress bio-oil (dry basis, wt%).

	Pennycress pyrolysis Oil	Pd/C A	Pd/C B	Pt/C	Ru/C A ^a	Ru/C B
Carbon	68.42	73.68	74.11	67.88	75.77	73.92
Hydrogen	7.84	9.59	9.56	9.37	10.07	10.25
Nitrogen	8.53	7.86	6.31	5.59	7.86	6.10
Sulfur	0.56	0	0	0	0	0
Oxygen	14.65	9.27	9.57	17.16	7.34	9.40
C:O (mol)	4.20	10.60	10.33	5.27	13.77	10.49
C:N (mol)	9.72	10.93	13.71	14.16	11.25	14.14
H:C (mol)	1.45	1.50	1.55	1.66	1.66	1.66
HHV (MJ/kg)	31.0	33.4	37.3	35.3	37.0	36.1
TAN (mg KOH/g)	84	16	17	16	12	10

^a Top organic phase.

Table 3
Elemental analysis of hydrogenated white-oak pyrolysis-oil (dry basis, wt%).

	White oak pyrolysis oil	Pd/C A	Pd/C B	Pt/C	Ru/C A	Ru/C B
Carbon	57.29	64.08	62.87	61.97	62.97	62.87
Hydrogen	6.85	8.09	9.09	9.42	9.79	9.09
Nitrogen	0.19	0.24	0.25	0.25	0.28	0.25
Sulfur	0	0	0	0	0	0
Oxygen	35.67	28.37	27.78	28.37	26.96	22.94
C:O (mol)	2.14	3.09	3.01	2.91	3.11	3.88
H:C (mol)	1.44	1.52	1.74	1.82	1.87	1.78

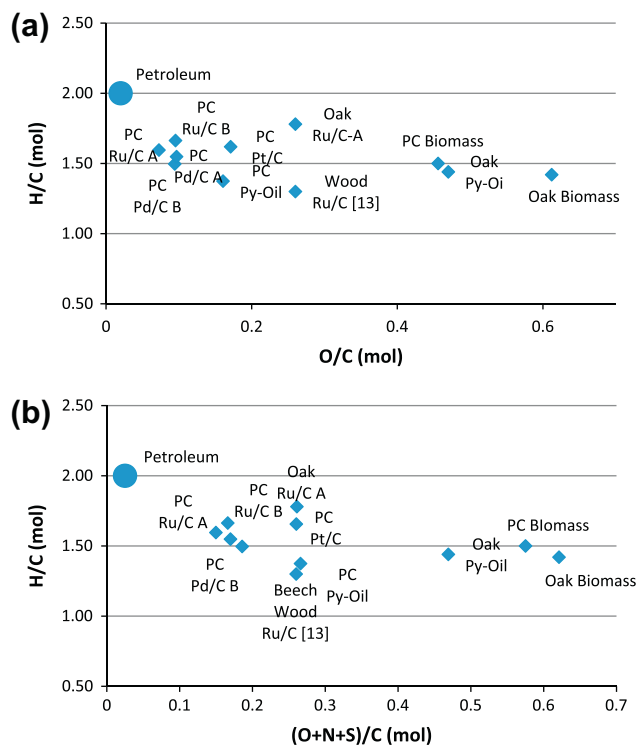


Fig. 1. Van Krevelen type diagrams comparing wood and pennycress biomass, pyrolysis oils, and hydrotreated products over various catalysts. Petroleum is added for comparison. (a) traditional diagram accounting for hydrogen and oxygen contents (b) a modified diagram accounting for total heteroatom (O, N, and S) content.

high nitrogen content must be mitigated, either in a refinery process or in a separate step.

The great majority (90–99%) of the gas collected at the conclusion of the experiments was unreacted H₂. The composition of the reaction by-product gas that makes up the remaining portion of the gas collected is presented in Fig. 2. The largest component of

this is CO making up 70–90% of the produced gas. This is in contrast to the results reported for the hydrotreating of wood pyrolysis oils where CO₂ is the most abundant gaseous by-product. CO₂ is produced from the decarboxylation of organic acids which are much less abundant in pennycress presscake pyrolysis oils than they are in beech wood pyrolysis oil [13], accounting for the decrease in observed CO₂ formation. CO was least concentrated in the case of the Ru-A catalyst which was most effective for deoxygenation. Combined with the low yield of gas observed for this catalyst, this trend is consistent with the observations on the liquid fraction because CO formation is not productive in reducing the C/O ratio of the pyrolysis oil. Other gaseous species produced were mostly saturated light hydrocarbons (CH₄, C₂H₆, and C₃H₈), ethylene and propylene were detected but only in trace quantities, except in the case of Ru-A where it was detected in a measurable amount. The co-products of the HDN, and HDS reactions ammonia and hydrogen sulfide were also detected, but not quantified.

The chemical nature of the upgraded pennycress presscake pyrolysis oils was analyzed by two-dimensional GC coupled with mass spectroscopy (GC × GC/MS) and ¹H and ¹³C NMR. The GC × GC analysis was done on the small scale reactions as described in the methods section. A GC × GC chromatogram of the

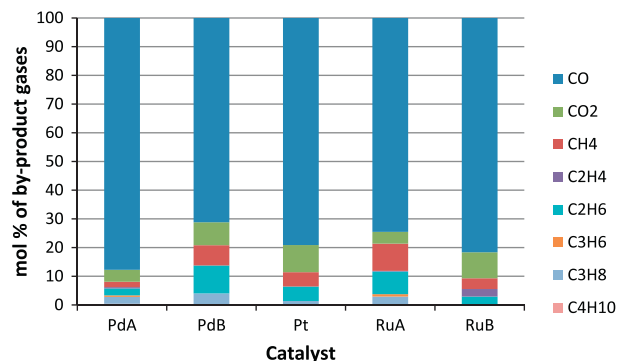


Fig. 2. Composition of gas by-product from hydrotreating of pennycress presscake pyrolysis oils over different catalysts.

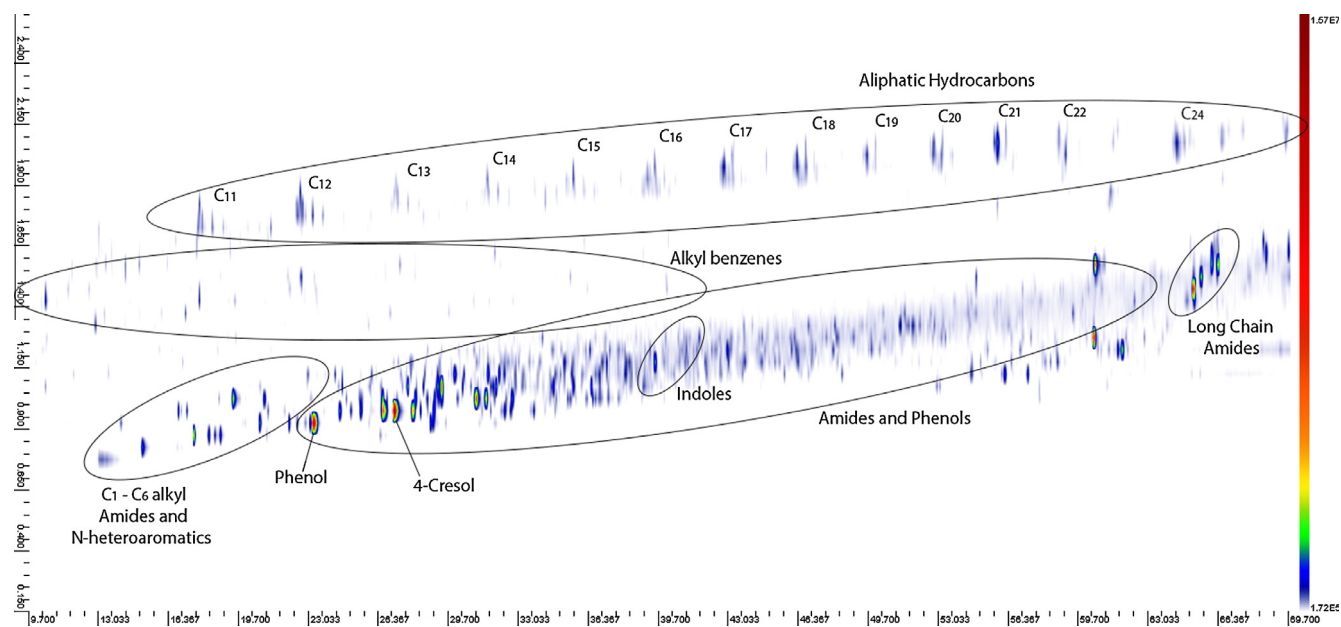


Fig. 3. GC × GC chromatogram of hydrotreated pennycress presscake pyrolysis oil.

product produced via hydrogenation over Ru-A is given as an example in Fig. 3. The upgraded products are extremely complex mixtures, perhaps more complex than the pyrolysis oil starting material, with up to 699 different compounds detected by GC × GC with 567 being the average number of compounds detected among the five catalysts studied. Generally, the most abundant compounds in the upgraded products are alkyl amides, N-aromatics, phenols and aliphatic and aromatic hydrocarbons. Many alkyl amides of various alkyl chain lengths on both the N and C sides (R and R') of the amide functionality are detected.

These vary from the simplest case of acetamide to amides containing very long chains at either R or R' and also includes cyclic amides (e.g. piperidone and derivatives).

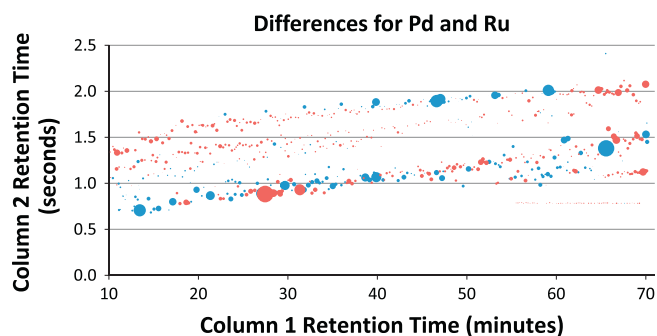
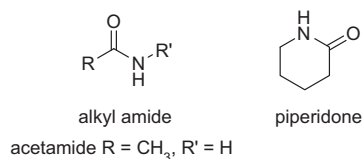


Fig. 4. Comparison of the relative abundance of individual compounds in pennycress presscake pyrolysis oils hydrotreated over Pd/C and Ru/C catalysts. Red dots represent peaks larger for Pd catalysts and blue for peaks larger for Ru catalysts. The area of the peak represents the magnitude to the difference. Refer to Fig. 3 for reference of compound classes.

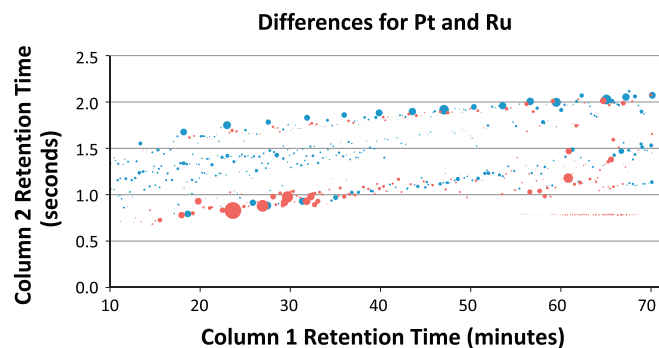


Fig. 5. Comparison of the relative abundance of individual compounds in pennycress presscake pyrolysis oils hydrotreated over Pt/C and Ru/C catalysts. Red dots represent peaks larger for Ru catalysts and blue for peaks larger for Pt catalysts. The area of the peak represents the magnitude to the difference. Refer to Fig. 3 for reference of compound classes.

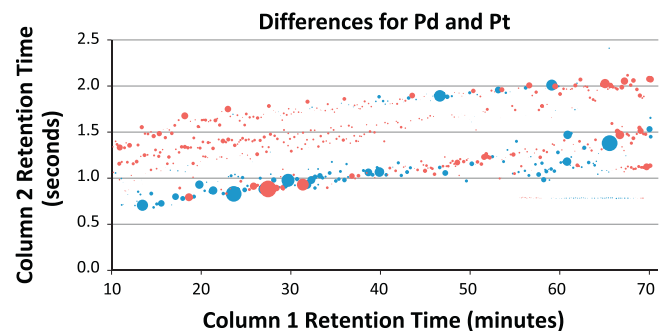


Fig. 6. Comparison of the relative abundance of individual compounds in pennycress presscake pyrolysis oils hydrotreated over Pd/C and Pt/C catalysts. Red dots represent peaks larger for Pt catalysts and blue for peaks larger for Pd catalysts. The area of the peak represents the magnitude to the difference. Refer to Fig. 3 for reference of compound classes.

These compounds account for a significant amount of the N and O content that remains in the upgraded oil, although N-heteroatomics and phenols were also detected. These remaining heteroatom groups are reduced in number, generally less protic and polar than those found in the untreated pyrolysis oil and are largely associated with long hydrocarbon chains. Therefore, the compatibility of the liquids with hydrocarbons in refinery blendstock will be highly increased. Some of the most intense individual compound peaks in the GC \times GC analysis are for phenol and cresol, and other alkyl phenols are detected as well. The phenols likely arise from partial HDO of the lignin fraction of the pyrolysis oil, a large abundance of phenols was reported for HDO of wood pyrolysis oils under similar conditions [12,13]. The phenolic compounds are also likely the source of the small amount of remaining acidic groups in these samples, indicating that although the relative abundance of these individual compounds is high, as a class of compounds (phenols) they are in low concentration.

To compare the compositions of the various products produced from upgrading over the different catalysts, the GC \times GC/MS chromatograms were subjected to comparative data comparison methods. Fisher ratio based pair wise comparisons between the chromatograms for each of the catalysts were made as described in the methods section [17–19]. Because there were minimal differences noted by the bulk analysis on the different charcoal supports, only comparisons of the three metals are made here. Figs. 4–6 compare chromatograms of between the Pd-A and Ru-A, Ru-A and Pt and Pd-A and Pt where the area of the mark for each compound indicates the magnitude of the difference in abundance for that peak. Interestingly, the products from the Pt catalyst had the highest abundance of both alkyl and aromatic hydrocarbons (those at the middle to highest retention times on the 2nd dimension column), although it was the least effective at oxygen removal. Pt was the best of the catalysts at rejection of nitrogen, although none of the catalysts were highly effective at nitrogen removal. This suggests that the greater direct source of the hydrocarbons de-

tected here may have been nitrogen containing compounds in the pyrolysis oil rather than oxygen containing compounds. Possibly, the hydrocarbons are directly formed from the prevalent alkyl amides, with the oxygen containing portion remaining in the liquid. This is further supported by the observation that alkyl amides are found in higher abundance for the products of the Ru and Pd catalysts. Between the Ru and Pd catalysts overall the differences are smaller although generally the alkyl amides are present in higher concentration for the products using the Ru catalyst and phenolics are more abundant for products of the Pd catalyzed hydrogenations. It is also important to note that the entire portion of the liquid products are not volatile enough to be detected by GC, so discrepancies between the observations in compounds detected by GC and heteroatom content could lie in this less volatile material.

NMR, both ^1H and ^{13}C , were used to further characterize the upgraded pyrolysis oils from pennycress presscake. A comparison of the ^1H NMR spectra of the pyrolysis oil and products from hydrotreating over Pd, Pt and Ru is given in Fig. 7. The percentage integrations of various spectra regions representing the abundance of hydrogen atoms associated with different functional groups is given Table 4. More than 50% of the hydrogen atoms in the pyrolysis oil hydrotreated over each of the catalysts resonate between 0 and 1.5. For the Pd-A and Ru-A a large peak at 1.35 ppm accounts for a large portion of resonance in this region, suggesting an abundance of long alkyl chains. In the case of all of the catalysts the percentage of the hydrogen atoms closely associated with heteroatoms found between 3.0 and 6.0 ppm is decreased from the raw pyrolysis oil. As expected from the elemental analysis the products of the Ru and Pd catalysts have less of these types of hydrogens than does the product from the Pt catalyst. The abundance of aromatic protons decreases going from the raw pyrolysis oil to the upgraded products, suggesting that some hydrogenation of aromatic rings to saturated hydrocarbons does occur. A similar comparison of the ^{13}C NMR and quantitative integrals are given in Fig. 8 and

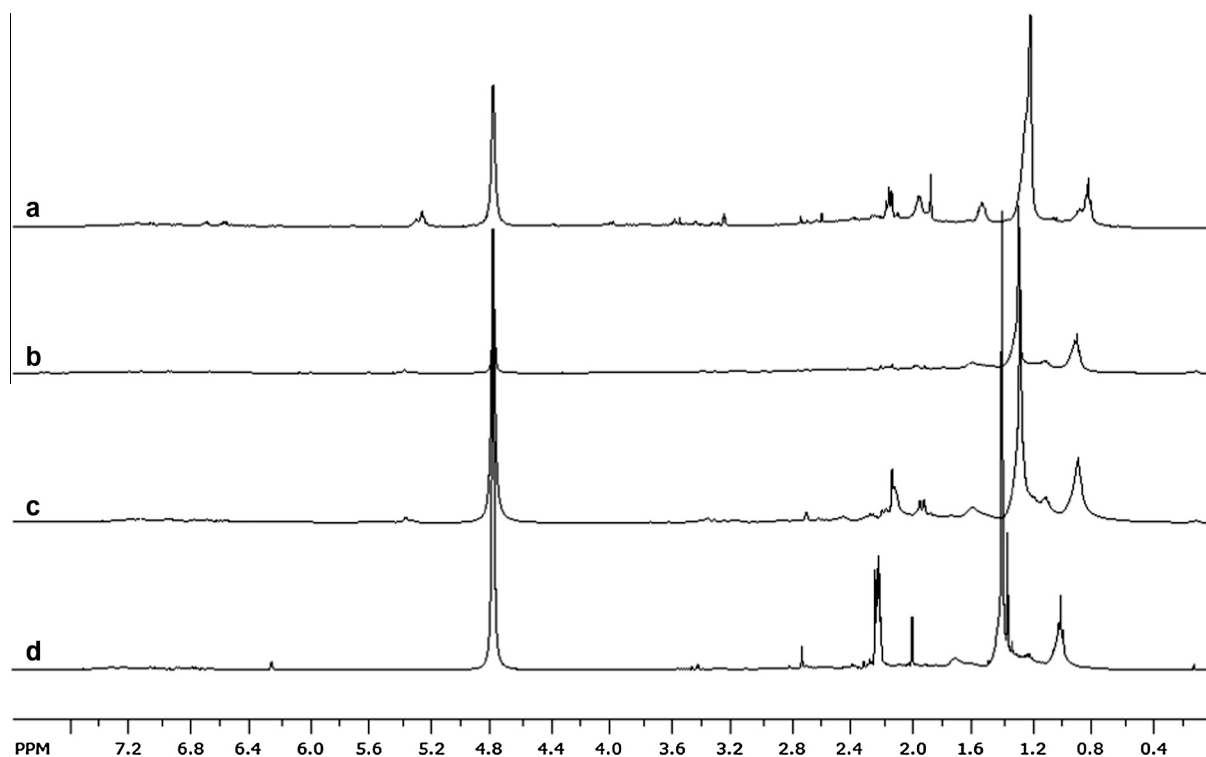


Fig. 7. ^1H NMR spectra (400 MHz, methanol- d_6) of pennycress presscake pyrolysis oil (a) and its hydrotreated products over Ru/C-A (b), Pd/C-A (c) and Pt/C (d).

Table 4
¹H NMR integrations (%) for hydrotreated pyrolysis oils of pennycress presscake.

Chemical shift	Pyrolysis oil	Pd/C A	Pt/C	Ru/C A
0.5–1.5 Alkanes	42.5	60.3	54.9	55.2
1.5–3.0 Aliphatic β-to O or N, α-to benzene ring	41.3	31.7	39.0	36.3
3.0–4.4 Alcohols, amines	6.0	1.7	2.3	3.9
4.4–6.0 Methoxy, carbohydrates, phenolic –OH	4.8	0.8	0.1	0.7
6.0–8.5 Aromatics (including heteroaromatics)	5.4	5.4	3.7	3.9

Table 5. The shift from aromatic to aliphatic character is more evident from the ¹³C NMR with percentage of aromatic carbon in the sample decreasing from 40% in the pyrolysis oil to about 11% in the product of upgrading over Ru-A and Pd-A. Aromatic carbon was slightly more abundant in the products from the hydrogenation over the Pt catalyst, consistent with observation of higher levels of aromatics in the GC × GC analysis. A large amount of the carbon (>70%) is found in aliphatic chains (0–55 ppm) for the products from each of the catalysts, compared to only ~45% for the pyrolysis oil starting material. For each of the upgraded products the number of peaks associated with carbon adjacent to oxygen (55–95) is decreased although the total percentage of the carbon is relatively similar. Interestingly, there is a higher percentage of the carbon found in the 0–28 ppm region where methyl and methylene groups of isolated aliphatics are found for the less effective Pt catalysts compared with the Ru-A or Pd-A catalysts, where more carbon is found in the 28–55 region with a large peak at ~30 ppm. This suggests that there are more methyl groups and smaller chains in the product of the Pt catalysts than that from the Ru-A or Pd-A catalysts. This is consistent with the observation of a higher abundance of GC × GC observable hydrocarbons for the Pt-catalysts. Conversely it suggests there is a larger presence of very long

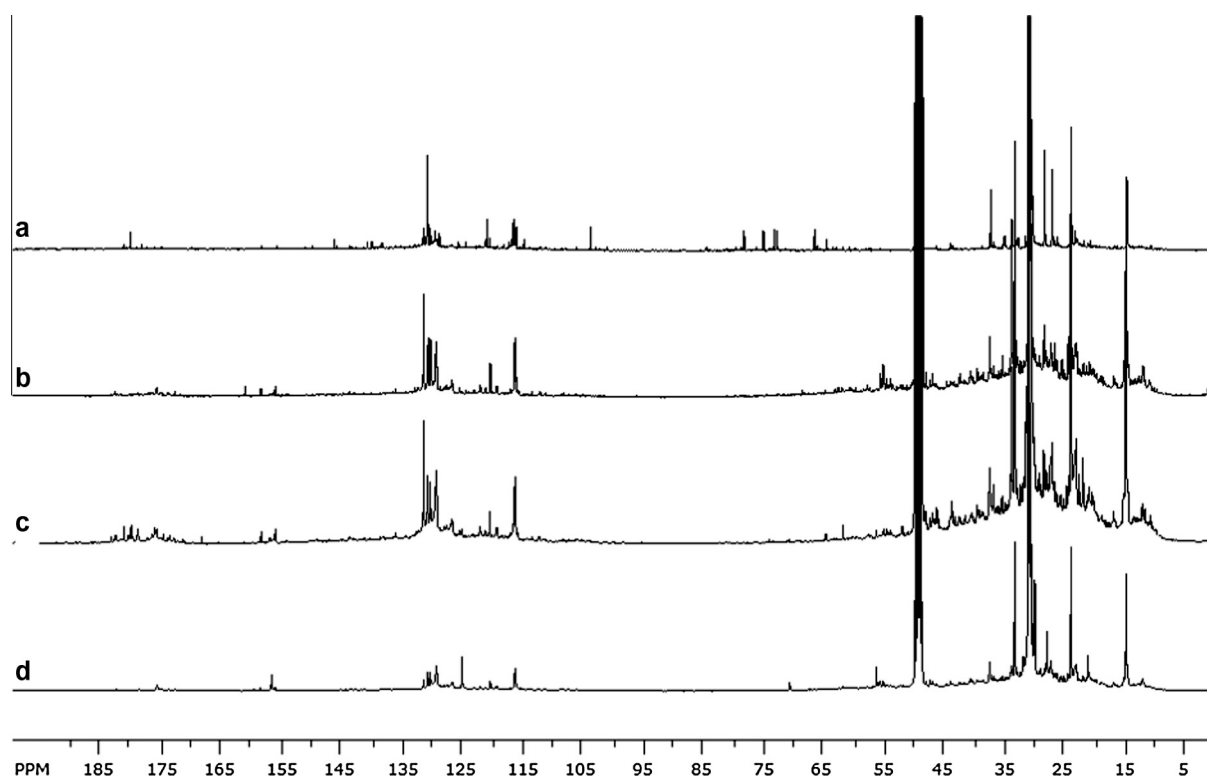
Table 5
¹³C NMR Integrations (%) for hydrotreated pyrolysis oils of pennycress presscake.

Chemical shift	Pyrolysis Oil	Pd/C A	Pt/C	Ru/C A
0–28 Isolated aliphatics	36.0	34.4	46.1	30.5
28–55 Long chain aliphatics, α to N	9.2	47.7	32.3	46.8
55–95 α to O	7.9	5.4	4.6	10.0
95–165 Aromatics (including heteroaromatics)	40.4	10.4	14.1	11.6
165–180 Amide RHN-C=O, acids, esters C=O(OR)	5.3	1.8	0.5	1.1
185–215 Carbonyls	1.2	0	0.1	0

chains in the products of the Pd-A and Ru-A catalysts. There is also a larger diversity of peaks in the aliphatic region for the products of the Pd-A and Ru-A catalysts compared with the raw pyrolysis oil or the product of the Pt-catalysis. There is also a decrease in the resonances between 165–180 ppm for each of the catalytic process, reflective of the decrease in acid content. The remaining amount of carbon signals in that region are the NC=O of the amides that were detected in large amounts by GC × GC; the Pd-catalysts produced the most diversity in carbons of this type.

4. Conclusions

The hydrotreating of pennycress presscake pyrolysis oils over Ru/C and Pd/C was effective for further reducing the oxygen content of pyrolysis oils from pennycress presscake. The pyrolysis oil from pennycress presscake, like those from other proteinaceous biomass is inherently deoxygenated compared with those from highly lignocellulosic biomass such as wood or herbaceous species. Use of Pt/C was less effective for hydrodeoxygenation (HDO) but slightly more effective for hydrodenitrogenation (HDN) than Pd or Ru catalysts. All catalysts performed complete hydrodesulfurization (HDS) of

**Fig. 8.** ¹³C NMR spectra (100 MHz, methanol-d₆) of pennycress presscake pyrolysis oil (a) and its hydrotreated products over Ru/C-A (b), Pd/C-A (c) and Pt/C (d).

the pyrolysis oil. The composition of the upgraded products was studied by GC × GC/MS and NMR. Compositionally, the upgraded products from hydrotreating over Ru/C or Pd/C catalysts were rich in long alkyl chains and had low aromatic content (~1% of carbon). The most abundant nitrogen and oxygen containing species remaining in the upgraded products and detected by GC × GC/MS were alkyl amides. Overall, the hydrotreated products from pennycress presscake had composition and energy contents closer to that of petroleum than did the similarly upgraded products from oak or beech wood; this demonstrates the potential advantage of utilization of proteinaceous biomass in pyrolysis conversion processes.

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