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Analysis and Comparison of Bio-Oil Produced by Fast Pyrolysis from Three Barley Biomass/Byproduct Streams

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Fluidized-bed fast pyrolysis was carried out on three different barley biomass coproduct streams, straw, hulls, and distiller's dried grains with solubles (DDGS), from *Saccharomyces cerevisiae* fermentation of barley grain. Each of these byproducts of fuel ethanol production from barley grain is a possible source of feedstock for advanced biofuels production via fast pyrolysis. Bio-oil recovery was in the range of 42−50 wt % of the biomass, but optimized yields could be as much as 70 wt % for each feedstock when the mass balance is mathematically adjusted to account for all unrecovered products using optimization modeling. Biochar yields were 16−21% from the barley feedstocks. Bio-oil produced from straw and hulls had an energy content of 24−25 MJ/kg on a dry basis, while bio-oil produced from DDGS had a dry basis energy content > 30 MJ/kg. The bio-oils were further characterized for composition and stability. None of the bio-oils were found to be shelf-stable, as established by an increase in average molecular weight when stored under accelerated aging conditions, a result which is typical for biomass fast pyrolysis bio-oils. Stability was best for the bio-oils produced from straw and hulls and worse for bio-oil produced from the DDGS. The results indicate that colocating a fast pyrolysis unit in a barley ethanol plant may produce potentially usable and blendable liquid fuel from any byproducts of the barley processing value chain.

Introduction

Barley is the fourth most produced cereal grain in the world, with 133 million tons grown worldwide in 2007.[1] Most of this barley is used for animal feed or malting; however, recently, interest has grown in using the grain to produce fuel ethanol by fermentation,[2] especially in the Mid-Atlantic and Southeastern United States, areas outside the Corn Belt. In these areas, barley can be grown as a winter crop, so that it does not interfere with production of traditional food crops grown in these areas. Double-cropping in this manner has the added benefit of reducing soil erosion and nitrogen leaching, major concerns for areas within costal watersheds such as the Chesapeake Bay area.[3,4] Should the barley-to-ethanol industry mature, production and utilization of winter barley for ethanol production will produce a wide variety of biomass streams in the value chain including straw, hulls, and distiller's dried grains with solubles (DDGS) that can be used as feedstock for the production of advanced biofuels. Although DDGS has more value as animal feed than as a feedstock for biofuel, DDGS produced from barley with higher levels of mycotoxin contamination may best be utilized otherwise. Biofuel is one viable option for its utilization and disposal.[5]

This study examined the thermochemical conversion of the straw, hulls, and DDGS barley biomass streams by fast pyrolysis to produce bio-oil (pyrolysis oil) and biocharcoal. The fast pyrolysis process results in the depolymerization of the biomass components into condensable vapors that make up bio-oil. The process could potentially be a safe method of disposal of toxin-contaminated feedstocks which, otherwise, are waste. Our selection for the pyrolysis conversion technology for these streams stems from the fact that bio-oil might be used as a boiler fuel "as is" in colocated ethanol plants, or it can be upgraded to transportation fuels.[6,7] Pyrolysis also offers the advantage of simultaneously producing a solid biocharcoal coproduct, which can be used as a soil amender that sequesters carbon for millennia, prevents soil erosion, and prevents nutrient leaching.[8,9] Unlike some of the existing biochemical conversion technologies, such as fermentation to ethanol, pyrolysis is amenable to a smaller-scale with the potential for farm scale operations.[10] This could complement an integrated barley-to-ethanol plant fed by barley farms with distributed pyrolyzers to convert the straw and hulls to the fuel intermediates, and the biocharcoal could be returned to those

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Table 1. Process Conditions for the Experimental Runs[a]

	straw 1	straw 2	hulls 1	hulls 2	DDGS 1	DDGS 2
run date	11/4/08	11/18/08	7/30/08	8/4/08	3/27/09	4/3/09
biomass [g]	3000	1240	2466	2920	1815	1935
feed rate [g/h]	1260.50	1265.31	1058.37	1649.72	1296.4	1935.0
bed temp. [°C]	500.20	484.70	496.80	494.50	498.3	490.3
condenser #1 temp. [°C]	285.50	296.90	235.20	256.40	276.4	282.4
condenser #3 temp. [°C]	138.2	116.9	142.7	139.3	115.6	141.2
condenser #4 temp. [°C]	34.6	30.7	49	40.9	43.0	42.2
ESP temp. [°C]	23.2	21.4	40	28.5	28.6	27.1

[a] Temperatures were not measured for condenser #2.

farms, for use as a soil amender. Despite the growing interest in pyrolysis liquids produced from agricultural residues, bio-oil production from barley biomass streams has not been previously studied. To date, studies on the pyrolysis of barley biomass have been limited to analytical studies using thermogravimetric analysis or analytical pyrolysis-gas chromatography (py-GC) methods.[11,12]

In this study, pilot-scale fast pyrolysis of three products from the barley production supply chain are compared. Detailed characterization and comparisons of the bio-oils including yields and compositions, as well as mass and energy balances of the production system, are discussed.

Methods and Materials

Feedstock. The barley straw and barley hulls feedstocks were of the Thoroughbred barley variety grown in Virginia and harvested in 2007. The hulls were obtained from dehulling of the barley grain at Montana Milling (Great Falls, MT). The DDGS was unique; it was a coproduct recovered after fermentation of the hull-less barley grain of the variety "Eve" grown in Virginia and harvested in 2005. Each of these potential pyrolysis feedstocks was ground in a Wiley mill with a 2 mm screen and dried overnight at 60 °C prior to subjecting them to fluidized-bed pyrolysis.

Fluidized-Bed Fast Pyrolysis. Fast pyrolysis was carried out in a bubbling fluidized bed of quartz sand at temperatures of ~500 °C. The pyrolysis system was previously described in detail by Boateng et al.[13,14] The system comprised a 7.5-cm- (3-in.-) diameter fluidized-bed reactor section, followed immediately by two cyclones to remove biocharcoal. The pyrolysis vapors are condensed by a series of four condensers cooled by cold water (~4 °C), and the remaining aerosols are collected by a bank of three electrostatic precipitators (ESPs) that capture a large fraction of the pyrolysis oil produced. Temperature and pressure measurements were collected and recorded using a Labview data acquisition and control system (National Instruments). Table 1 presents the process conditions for each of the experimental runs. The noncondensable gas (NCG) was analyzed by gas chromatography (GC) (Agilent MicroGC 3000A) and quantified versus a standard mixture of gases containing 4 mol % each of CO_2, CO, H_2, CH_4, C_2H_6, and C_3H_8 with the balance being N_2. After product characterization and analysis, as described in the following sections, the energy balance of the pyrolysis system was established.

Yield Determination. The recovery of bio-oil and biocharcoal was determined gravimetrically, which for several reasons, including short run times and the high viscosity of bio-oil, results in a large imbalance where overall mass closure is only 60−70%. A nonlinear programming optimization model was developed to adjust the experimental data to achieve closed balances without losing the overall representation of the pyrolysis process and within the law of conservation of mass.[15] The model adjusts the amounts of seven pyrolysis products, bio-oil (organic), biocharcoal, water, CO_2, CO, CH_4, and H_2, subject to several constraints (e.g., measured ratios of permanent gases are set, and measured amounts of bio-oil, water, and biocharcoal are set as minimums), such that the amount of carbon, oxygen, hydrogen, and ash is conserved from the biomass to the pyrolysis products. The resultant total of CO_2, CO, CH_4, and H_2 is considered as NCG.

Product Characterization. Bio-oils were analyzed as two fractions, (i) that collected at the ESP and (ii) "whole" bio-oil, prepared by mixing all of the fractions from the condensers and the ESP in the proportion in which they were recovered. Bio-oil−water content was determined by Karl Fischer (K−F) titration using 3:1 methanol/chloroform as a solvent and HYDRANAL Karl Fischer Composite 5 (Fluka) as a titrant. Calorific values of the feedstock, bio-oil, and biocharcoal were determined using a Parr 1281 bomb calorimeter. Elemental analyses (C, H, N, S) of the feedstocks and products were determined using a Thermo Flash EA1112 CHNS/O analyzer, by complete combustion of the material followed by GC quantification of the combustion products. Oxygen was then determined by difference after accounting for CHNS and ash. Ash was determined as the percentage remaining after heating a sample in a muffle furnace in air to 650 °C for 6 h. Bio-oil viscosity was measured using a Grabner MiniVis II Automatic Microviscometer. Bio-oil pH was measured with a Thomas Scientific 675 pH/ISE meter at ambient temperature.

Gas chromatography with mass spectroscopy detection (GC/MS) analysis of bio-oil was performed on an Agilent 6890N GC equipped with an Agilent 5973 mass selective detector. The column used was a DB-1701, 60 m × 0.25 mm in size and with a 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 to hold at 280 °C for 20 min. The injector temperature was 250 °C and the injector split ratio set to 30:1. The flow rate of the He carrier gas was 1 mL/min. The bio-oil samples for GC analysis were prepared as 6 ± 1 wt % solutions in acetone, which were filtered through a 0.45 μm PTFE filters prior to injection. Compounds were identified by comparison of their mass spectra with the NIST library. For quantification of individual bio-oil compounds (those indicated in Table 7), response factors relative to the internal standard, fluoranthene, were determined using authentic compounds.[16] The relative response factors of each compound were consistent over a range of concentrations that reflected those found in the samples.

Aqueous HPLC analysis of the bio-oils was used to quantify acetic acid, acetol, and levoglucosan because of difficulty quantifying these compounds by GC/MS. A Waters Breeze

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HPLC system using a refractive index detector, set at 30 °C, was used. The mobile phase was 0.007 N H_3PO_4. The column used was an Aminex HPX-87H, 300 × 7.8 mm in size (Bio-Rad, Inc.), and was heated to 30 °C. The pump was programmed for a flow rate of 0.6 mL/min and *n*-propanol was used as the internal standard for quantification.[16]

The water-insolubles were determined by mixing ~2 g of whole bio-oil with 100 mL of warm water (~35 °C), shaking vigorously, and filtering through 1 μm pore glass fiber filter. The filtrate was then washed several times with water. Water-solubles were calculated by difference. Hexane extraction was carried out to produce samples for HPLC lipid analysis (see below) by adding 30 mL of hexane to 2 g of bio-oil, mixing for 1 h, and decanting the extract. An additional 30 mL of hexane was added and stirred overnight, decanted, and added to the previous extract.[16] After further rinsing with hexane, the solvent was removed by rotary evaporation at reduced pressure.

Nonpolar lipid classes found in the bio-oil were analyzed by HPLC according to a previously reported method.[17] The HPLC used was an Agilent Model 1100 with an autosampler. The detector was an ESA Corona Charged Aerosol Detector (ESA Biosciences, Chelmsford, MA) operated with nitrogen as a nebulizing gas and at a range of 500 pA. A LiChrosorb 7 μm DIOL column (3 × 100 mm, packed by Chrompack, Raritan, NJ) was used. The binary gradient had a constant flow rate of 0.5 mL/min, with solvent A = 99.9% hexane/0.1% acetic acid (all solvent compositions are v/v) and solvent B = 99% hexane/1% isopropanol. Gradient timetable: at 0 min, 100/0 (%A/%B); at 8 min, 100/0; at 10 min, 75/25; at 40 min, 75/25; at 41 min, 100/0; and at 60 min, 100/0. These nonpolar lipid components were identified by comparison to the retention times of commercial standards.

Polar lipids found in the bio-oil hexane extracts (including glycolipids and phospholipids) were quantitatively analyzed by a similar HPLC-ELSD method,[18] using a Hewlett-Packard Model 1100 HPLC, with autosampler, and detection by both an HP model 1100 diode-array UV−visible detector (Agilent Technologies, Avondale, PA) and a Sedex Model 55 Evaporative Light Scattering Detector (Richard Scientific, Novato, CA), operated at 40 °C and a nitrogen gas pressure of 2 bar. The diol column and flow rates were the same as above. The ternary gradient consisted of solvent A = hexane/acetic acid, 1000/1; solvent B = isopropanol; and solvent C = water. Gradient timetable: at 0 min, 90/10/0 (%A/%B/%C); at 30 min, 58/40/2; at 40 min, 45/50/5; at 50 min, 45/50/5; at 51 min, 50/50/0; at 52 min, 90/10/0; and at 60 min, 90/10/0. The minimum limits of quantitative detection with both HPLC methods were about 1 μg per injection. Mass versus peak area calibration curves were constructed for the range of 1−20 μg per injection.

Gel permeation chromatography (GPC) analysis of bio-oil was performed using a Polymer Laboratories GPC-50 (Varian, Inc.). Two identical Oligo-Pore GPC columns (polystyrene−divinylbenzene copolymer, 300 × 7.5 mm) in series were used at 35 °C, and THF was used as the mobile phase at a 1 mL/min flow rate. Samples were dissolved (~1 mg/mL) in THF and filtered through a PTFE filter prior to use. Peak detection was done by refractive index. The GPC columns were calibrated using six polystyrene standards in the MW range of 162−2900. Accelerated aging was done by storage of the bio-oil in a sealed vial in an oven at 90 °C using a procedure modified from Oasmaa and Kuoppala.[19]

Results and Discussion

We present a comparison of some of the key analyses of the feedstock, pyrolysis process yields, and energy use and product analysis including differences in composition and bio-oil stability. The potential for extracting compounds such as lipids from the bio-oil by hexane extraction is also reported and discussed.

Table 2. Analysis of Biomass Samples used for Pyrolysis

	as received	dry basis	dry, ash free
	Barley Straw		
moisture (wt %)	1.37		
ash (wt %)	2.34	2.37	
C (wt %)	46.22	46.86	48.00
H (wt %)	6.07	6.15	6.30
N (wt %)	0.77	0.78	0.80
S (wt %)	0.15	0.15	0.15
O (wt %)	43.10	43.69	44.76
C/O ratio (mol)	1.43:1	1.43:1	1.43:1
HHV (MJ/kg)	16.2	16.6	16.8
	Barley Hulls		
moisture (wt %)	3.00		
ash (wt %)	6.03	6.22	
C (wt %)	42.89	44.21	47.14
H (wt %)	5.65	5.82	6.21
N (wt %)	0.99	1.03	1.09
S (wt %)	0.00	0.00	0.00
O (wt %)	41.44	42.73	45.56
C/O ratio (mol)	1.38:1	1.38:1	1.38:1
HHV (MJ/kg)	17.1	17.6	18.8
	Barley DDGS		
moisture (wt %)	2.33		
ash (wt %)	4.56	4.67	
C (wt %)	49.96	51.15	53.66
H (wt %)	6.92	7.09	7.44
N (wt %)	4.31	4.42	4.63
S (wt %)	0.52	0.54	0.56
O (wt %)	31.39	32.14	33.71
C/O ratio (mol)	2.12:1	2.12:1	2.12:1
HHV (MJ/kg)	20.8	21.3	22.3

Biomass Feedstock Characterization. On a compositional basis, the barley straw and hulls, while compositionally different, are comprised of varying proportions of five major classes of cell wall compounds: cellulose, hemicellulose, and lignin and relatively smaller amounts of protein and lipids. We find that the proportions of these classes are similar to those found in wood, herbaceous grasses, and other lignocellulosic biomass feedstocks traditionally considered for cellulosic biofuels production.[6,7] The DDGS composition was very different from those of the other two feedstocks, distinguished by its high protein content (33.7 wt %) and its relativity high oil (triglyceride) content at 6.0 wt %, compared to the barley hulls, which also contained a detectable amount of oil, 2.2 wt %. The elemental analyses of the feedstocks used in this study are shown in Table 2. As seen, the ash content (as received) of the hulls (6.0 wt %) was highest, followed by DDGS (4.6 wt %) and straw (2.3 wt %). This is important because the ash is concentrated into the biocharcoal during pyrolysis and, as such, can catalyze changes in the biopolymer decomposition pathways during pyrolysis.[6,7] Among the three feedstocks, the DDGS has the highest C/O ratio corresponding to its highest energy content at ~20 MJ/kg. Although the straw and hulls have similar compositions, the latter had a slightly higher C/O ratio and thereby slightly higher energy content, that is, 17 MJ/kg and 16 MJ/kg, respectively. Owing to its high protein content, the DDGS had a much higher nitrogen content than did the barley straw or hulls.

Bio-Oil Production and Yields. The process conditions for each of the pyrolysis experiments are shown in Table 1. Each of the feedstocks was fed at a rate of 1−2 kg/h, pyrolyzed at

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Table 3. Elemental Analysis (Dry Basis, wt%), High Heating, pH, and Viscosity Values of Bio-Oil[a]

biomass bio-oil fraction	straw ESP	straw whole	hulls ESP	hulls whole	DDGS ESP	DDGS whole
C	57.02	50.78	56.80	54.73	60.14	74.02
H	6.64	3.20	5.91	5.32	6.74	8.92
N	1.08	1.37	1.54	1.79	8.00	5.05
S	0.00	0.00	0.00	0.09	0.67	0.35
O	29.51	44.42	36.45	38.49	24.44	6.24
C/O ratio (mol)	2.58:1	1.52:1	2.07:1	1.89:1	3.27:1	15.82:1
water content (wt%)	6.6	26.7	6.5	13.8	13.4	18.7
HHV (MJ/kg, wet basis)	24.6	17.7	23.7	20.8	24.1	27.1
HHV (MJ/kg, dry basis)	26.3	24.2	25.5	24.1	27.7	32.9
pH[b]		2.4		2.5		6.5
viscosity (cSt, @ 40 °C)[b]	542	23.5	1302	102	249	277

[a] Average of the two bio-oils produced for each feedstock. [b] pH measured for whole bio-oil only.

Table 4. Analysis of Bio-Char[a]

	as-received	dry basis	dry, ash-free
	Barley Straw		
moisture (wt %)	1.19		
ash (wt %)	20.67	20.90	
C (wt %)	65.79	66.57	84.48
H (wt %)	2.67	2.71	3.43
N (wt %)	0.91	0.92	1.16
S (wt %)	0.00	0.00	0.00
O (wt %)	8.78	8.90	10.93
C/O ratio (mol)	10.0:1	10.0:1	10.3:1
HHV (MJ/kg)	24.2	24.7	31.0
	Barley Hulls		
moisture	1.92		
ash (wt %)	35.63	36.32	
C (wt %)	53.89	54.94	86.53
H (wt %)	1.80	1.84	2.99
N (wt %)	2.21	2.26	3.46
S (wt %)	0.00	0.00	0.00
O (wt %)	4.55	4.64	7.01
C/O ratio (mol)	15.8:1	15.8:1	16.5:1
HHV (MJ/kg)	18.0	18.6	31.4
	Barley DDGS		
moisture (wt %)	0.50		
ash (wt %)	33.50	33.67	
C (wt %)	51.35	51.61	77.77
H (wt %)	1.99	2.00	3.01
N (wt %)	4.47	4.49	6.76
S (wt %)	0.24	0.24	0.37
O (wt %)	7.96	8.00	12.09
C/O ratio (mol)	8.60:1	8.60:1	8.58:1
HHV (MJ/kg)	21.4	21.5	30.2

[a] Average of the two biochar samples produced for each feedstock, Table 4.

around 500 °C and quenched to below 300 °C at the first condenser. The vapors were cooled to nearly ambient temperature prior to final precipitation at the ESP. As described earlier, the pyrolysis system employed collects bio-oil at several different condensation points, accomplished by four cold-water chilled condensers and then a bank of electrostatic precipitators. For the purposes of bio-oil analysis, the composite of the four condensers was analyzed as one condenser-oil fraction and the composite of the bio-oil collected at the ESPs as the ESP-oil fraction. A composite of all fractions combined was analyzed as "whole" bio-oil. The reason for the latter characterization was to provide characterization independent of the collection method, as bio-oils produced industrially are usually collected as whole.

The yields of the bio-oil and biocharcoal were determined by weight and then corrected by applying a mass balance model (see Methods and Materials) using the elemental analyses of the feedstock and pyrolysis products (Tables 2−5).

Table 5. Composition of Noncondensable Gases (NCG)

gas (vol %)	straw	hulls	DDGS
CO_2	23.5	45.0	66.3
CO	55.5	48.1	25.8
CH_4	11.7	5.5	7.9
H_2	9.3	1.4	0.0
HHV (MJ/kg), dry, N_2 free basis	9.5	5.4	3.9

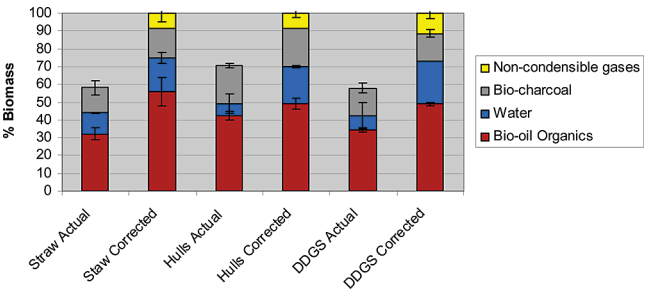

Figure 1. Pyrolysis product yields. Corrected values are based on a mass balance model (see Methods and Materials). Error bars represent one standard deviation.

The pyrolysis product yields are shown in Figure 1. An optimization mass balance model that accounts for all unrecovered products indicates bio-oil yield in the 70−75 wt % range (including water) for the pyrolysis of each of the three barley feedstocks, although only 42−49 wt % was physically collected. The model indicated that, for the pyrolysis of barley hulls and DDGS, water made up a large amount of the unrecovered material while more organic bio-oil went unrecovered for barley straw pyrolysis. The calculated result also indicates that the potential yield of organic bio-oil (bio-oil not including water) was highest for barley straw (56 wt %), followed by hulls (49 wt %) and DDGS (48 wt %). Biochar production was highest for the barley hulls (21 wt %), followed by barley straw and DDGS at about 16 wt %. NCG, which comprised mostly CO and CO_2 with small amounts of CH_4 and H_2, yields ranged between 8 and 11 wt %.

Elemental analysis and mass balance made it possible to determine how the elements in the biomass are distributed among the pyrolysis products (Table 6). This is especially useful in estimating the carbon conversion, a measure that determines the extent to which the energy contained within the biomass is converted to biofuel products. Of all of the carbon in the DDGS, 76.6% went to bio-oil, 16.2% to biocharcoal, and 7.3% to NCG . For barley straw, the carbon was distributed as 68.9% to bio-oil, 23.9% to biocharcoal, and 7.2% to NCG. For barley hulls, the distribution of its carbon was 65.4%, 27.6%, and 7.0% to bio-oil,

Table 6. Conversion of Biomass Organic C, H, O, N to Pyrolysis Products

	biomass	bio-oil	biochar	NCG	water
			Straw		
C	100%	68.9%	23.9%	7.2%	
H	100%	44.3%	7.2%	3.2%	33.7%
O	100%	47.7%	3.3%	12.7%	37.6%
			Hulls		
C	100%	65.4%	27.6%	7.0%	
H	100%	48.3%	6.7%	1.1%	39.8%
O	100%	42.4%	2.3%	13.0%	42.9%
			DDGS		
C	100%	76.6%	16.2%	7.3%	
H	100%	59.7%	4.4%	1.3%	36.9%
O	100%	10.4%	3.8%	24.0%	63.0%
N	100%	79.4%	20.7%		

biocharcoal, and NCG, respectively. The high carbon conversion to bio-oil for DDGS suggests that protein has a high rate of conversion to bio-oil compared with carbohydrates or lignin. A high rate of protein conversion to the liquid stream is further supported by the observation that 79% of the DDGS' nitrogen was recovered in the bio-oil product. Nitrogen in the bio-oil was found as organo-nitrogen bases (vide infra).

Like carbon, the distribution of oxygen and hydrogen could be similarly determined. In addition to conversion to organic bio-oil, biocharcoal, and NCG, a large amount of the feedstock O and H go to form reaction water that is partially dissolved in the bio-oil. Oxygen conversion to water is desirable because, combined with a high carbon conversion to bio-oil, it results in the deoxygenation of the organic bio-oil, without a loss of valuable carbon to CO or CO_2. This, in turn, results in bio-oil with a higher C/O ratio that will have a higher energy content. Deoxygenated bio-oil may also be more stable due to the lower concentration of reactive oxygenated functional groups in the bio-oil. The extent of which deoxygenation via production of water occurred varied with feedstock. The amount of organic oxygen contained in the feedstock converted to water was 38%, 43%, and 63% for straw, hulls, and DDGS, respectively (using the mass balance model calculated water yields). The bio-oil from barley straw had a molar C/O (excluding water) ratio of 1.5:1, from hulls 1.9:1, and an order of magnitude higher for DDGS at 15.8:1. The high carbon conversion and low oxygen conversion to organic bio-oil from DDGS resulted in a much higher energy density for this bio-oil, that is, ~32 MJ/kg (dry basis), approximately 80% that of petroleum. Comparatively, the bio-oil from straw and hulls had an energy density of ~24 MJ/kg (dry basis), a value within the range found for pyrolysis oils from woods and herbaceous grasses.[6]

Bio-Oil Characterization. In the pyrolysis system used for this study, it is generally the case that most of the reaction water is concentrated in the bio-oil collected at the condensers, and the bio-oil collected at the ESP contains less water and is therefore homogeneous.[15,16] The condenser fractions of the bio-oil produced from the straw and the hulls contained 36% and 22% water, respectively, while the ESP fractions contained only ~6% water (Table 7). The water in the bio-oil produced from DDGS fractionated slightly differently, with the bio-oil collected at the condensers containing 21% water, while the bio-oil collected at the ESP contained 13% water. For straw and hulls, the ESP fractions of bio-oil were more viscous than the whole bio-oil likely because of the lower water content of the ESP fractions. For DDGS, the ESP fraction and whole bio-oil had similar viscosities (Table 7). For whole bio-oils, the bio-oil from the hulls was the most viscous, followed by DDGS and barley straw. This trend is likely the result of a combination of factors including the bio-oil−water content, composition, and the abundance of higher molecular oligomeric compounds. Visual observations indicated that the bio-oil collected at the ESP from the hulls and straw was homogeneous (one phase), while the two-phase DDGS bio-oil remained heterogeneous even with gentle heating.

GC/MS and HPLC were used to quantify 21 of the hundreds of compounds in the bio-oils produced from these barley streams. In addition to water, some of the highly water-soluble compounds found in the bio-oil were also found in higher concentrations in the condenser fraction of the bio-oil (Table 7). Acetic acid and acetol were found in high concentrations in the bio-oils from barley straw and hulls. Overall acetic acid concentration was ~8 wt % in both the bio-oil from the straw and hulls with an acetol concentration of 5−6 wt %. The concentration of these compounds was about double that in the condenser fractions than in the ESP fractions. No acetol was found in the DDGS bio-oil, and the acetic acid concentration was also marginal, < 1 wt %. However, several basic organo-nitrogen compounds that are the result of protein pyrolysis were observed in the GC/MS chromatogram of the DDGS bio-oil. Nitrogen bases identified in the DDGS bio-oil included indole, methyl indole, 2-pyrrolidinone, and 2,2,6,6-tetramethyl-4-piperidone among several others. The low concentration of acid and the presence of these nitrogen bases rendered the DDGS bio-oil pH neutral, with the pH measured at 6.5. The bio-oil from the straw and hulls was acidic, with measured pHs of 2.4 and 2.5, respectively, typical of bio-oils produced from wood or other herbaceous biomass.[6,7] Levoglucosan, an anhydrosugar produced from cellulose dehydration during pyrolysis was found in concentrations of 2−3 wt % for each of the bio-oils and even in higher amounts in the ESP bio-oil fraction than in the condenser fractions. Small, GC-observable, phenolic compounds derived from lignin were generally found in higher concentrations in the bio-oil produced from straw and hulls than that from DDGS, probably due to the low concentration of lignin in the DDGS. Guiaicolic (guiaicol, 4-methyl-2-methoxyphenol, isoeugeol) and syringolic (2,6-dimethoxyphenol) compounds were found in higher concentration in the bio-oil from hulls, while nonmethoxy substituted phenolics (phenol, cresols, etc.) were found in higher concentration in the bio-oil from straw. The majority of the lignin-derived bio-oil components are of higher molecular weight and cannot be observed by GC. These usually make up the majority of the water-insoluble phase of the bio-oil, also known as pyrolytic lignin.[6,7] Overall, water insolubles accounted for 18 wt % of the organic bio-oil from barley straw, 26 wt % of that from barley hulls, and 52 wt % of that from barley DDGS (Table 8). In the case of the bio-oil from DDGS, the large amounts of water insolubles are more likely derived from protein than from lignin because DDGS does not contain large amounts of lignin. Also included in the water-insoluble fraction were nonpolar compounds that were soluble in hexane. For each case, the hexane extractables accounted for ~10 wt % of the bio-oil collected at the ESP.

Because of the relatively high lipid (triglyceride) content (6 wt %) of the DDGS biomass, the hexane-soluble portion

Table 7. Concentration of Some Chemical Compounds in Barley Bio-Oils (wt %)[a]

compound	straw cond.	straw ESP	straw whole	hulls cond.	hulls ESP	hulls whole	DDGS cond.	DDGS ESP	DDGS whole
proportion of total bio-oil	69.4%	30.6%	100%	45.0%	55.0%	100%	67.3%	32.7%	100%
water[b]	35.62	6.64	26.73	21.61	6.48	13.78	20.81	13.42	18.73
Carbohydrate Derived Compounds									
acetic acid[c]	10.19	4.79	8.56	9.78	5.66	7.56	0.88	0.56	0.75
furfural	0.39	0.38	0.39	0.46	0.57	0.53	0.00	0.00	0.00
3-methyl-2-cyclopenten-1-one	0.15	0.19	0.16	0.10	0.10	0.10	0.00	0.00	0.00
4-hydroxy-4-methyl-2-pentantone	0.06	0.06	0.06	0.07	0.08	0.07	0.06	0.09	0.07
acetol[c]	7.44	3.88	6.31	5.94	3.72	4.79	0.00	0.00	0.00
levoglucosan[c]	0.92	4.79	2.06	1.46	4.53	3.15	1.94	2.75	2.24
Lignin Derived Compounds									
phenol	0.31	0.63	0.40	0.18	0.19	0.19	0.16	0.13	0.15
p-cresol	0.07	0.13	0.09	0.07	0.10	0.08	0.25	0.20	0.24
o-cresol	0.09	0.17	0.12	0.04	0.04	0.04	0.03	0.00	0.02
m-cresol	0.09	0.15	0.11	0.03	0.04	0.04	0.01	0.00	0.01
2,4-dimethylphenol	0.03	0.04	0.04	0.01	0.02	0.02	0.00	0.00	0.00
4-ethyl phenol	0.06	0.14	0.09	0.07	0.09	0.08	0.01	0.01	0.01
guaiacol	0.03	0.07	0.04	0.23	0.26	0.24	0.02	0.05	0.03
2-methoxy-4-methyl phenol	0.00	0.00	0.00	0.25	0.34	0.29	0.00	0.00	0.00
isoeugenol	0.03	0.06	0.04	0.16	0.33	0.25	0.00	0.00	0.00
2,-6 dimethoxy phenol	0.03	0.06	0.04	0.17	0.23	0.20	0.00	0.00	0.00
Protein Derived Compound									
indole	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.05	0.06
Lipids[d,e]									
free fatty acids		0.2			2.7			4.1	
diacylglycerides		0			0.9			3.0	
triacylglycerides		0.1			1.6			1.8	
fatty acid ethyl esters		0			0			0.9	

[a] Determined by GC/MS unless otherwise indicated. Average of two runs in all cases. [b] Determined by Karl Fischer titration. [c] Determined by aqueous HPLC. [d] Determined by organic HPLC. [e] Predominantly based on palmitic and linoleic acids.

Table 8. Bio-Oil (Whole) Water Solubility Profile[a]

	straw	hulls	DDGS
water	26.7%	13.8%	18.7%
water insolubles	12.9% (17.6%)	22.2% (25.8%)	42.0% (51.7%)
water-solubles	60.4% (82.4%)	64.0% (74.2%)	39.2% (48.3%)

[a] Numbers in parentheses are dry-basis values.

Table 9. Molecular Weight Changes of ESP Bio-Oils Using Accelerated Aging and GPC[a]

bio-oil	time at 90 °c (h)	M_n	M_w
barley straw	0	303	446
	8	335	520
	24	362	609
barley hulls	0	314	456
	8	329	518
	24	341	626
barley DDGS	0	224	325
	8	376	565
	24	insoluble	

[a] Average of two runs.

of this bio-oil was analyzed for lipid content by HPLC (with light scattering detection) and LC/MS. This hexane extract contained free fatty acids (~41 wt % total, with palmitic and linoleic as the predominant free fatty acids), diacylglycerides (~30 wt %), and triacylglycerides (~18 wt %). The presence of these long carbon chain lipids contributed to the high energy content of the bio-oil produced from DDGS. There were also small amounts of fatty acid ethyl esters (~9 wt % of hexane extract) detected. These were likely formed from the reaction of residual ethanol left in the DDGS with the triglycerides during pyrolysis. It is

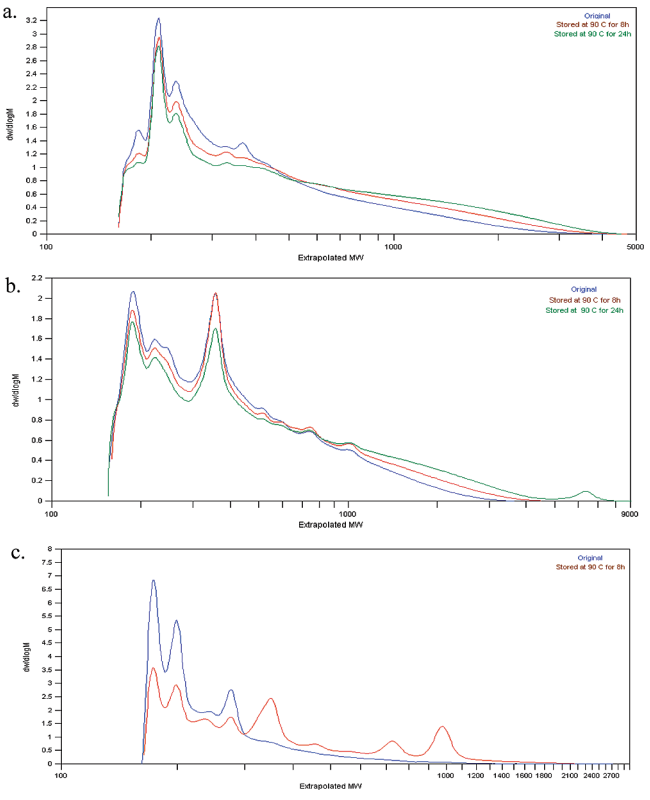

Figure 2. Molecular weight distribution (of compounds with $M_w \geq 162$) of the ESP fraction of bio-oil from (a) barley straw, (b) barley hulls, (c) barley DDGS. Unaged (blue), stored at 90 °C for 8 h (brown), and stored at 90 °C for 24 h (green). Bio-oil from DDGS was not soluble after storage at 90 °C for 24 h.

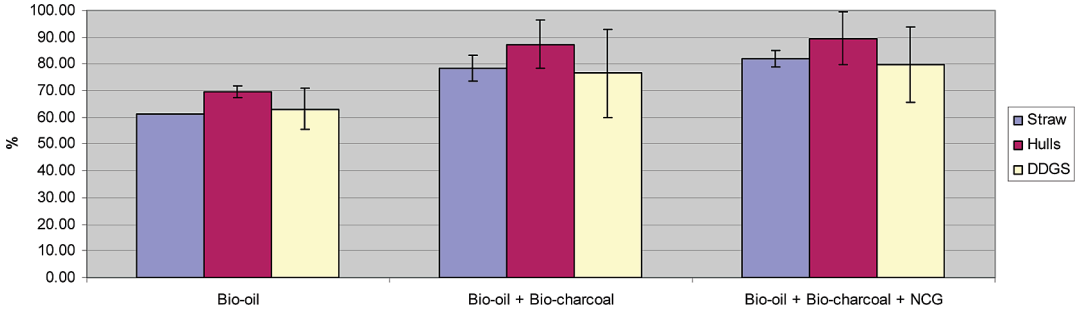

Figure 3. Energy efficiencies for the pyrolysis of barley biomass. Error bars represent one standard deviation.

also possible that free fatty acids produced during pyrolysis were esterified post-pyrolysis. Supporting the occurrence of the transesterification reaction was the observation that small amounts of glycerol were detected in the GC/MS of the DDGS bio-oil. When the hexane extract of DDGS was analyzed in a second (polar) HPLC system, only nonpolar lipids (mostly free fatty acids and diglycerides, as noted above) were detected. Although polar lipids (such as glycolipids and phospholipids) are commonly found in barley kernels, unrefined barley oil, and barley DDGS,[20] no polar lipids were detected in the hexane extract of barley DDGS, suggesting that any polar lipids are destroyed by fast pyrolysis.

The bio-oils were further characterized by gel permeation chromatography (GPC) which can provide molecular weight data on the highly oligomeric bio-oils and be used to monitor bio-oil stability on the basis of its average molecular weight. The number average molecular weights (M_n) of the ESP fractions of bio-oils were 303 for straw, 314 for hulls, and 224 for DDGS, and the weight average molecular weights (M_w) were 446, 456, and 325, respectively (Table 9). The values for straw agree well with previously reported values for similar biomass, for example, wheat straw.[21] All of the average molecular weight values are lower than those typically reported for wood pyrolysis oils, which typically fall in the range of Mn $\approx$ 330−380 and $M_w \approx$ 420−550.[22] GPC was also used to evaluate the stability of the bio-oils. Instability is a result of the fact that bio-oil undergoes a number of reactions during storage that increases their average molecular weight and viscosity.[21−23] These reactions are due to the high concentration of reactive functional groups such as carboxylic acids, ketones, and aldehydes. Instability is a major factor limiting the use of bio-oils as combustion fuel or an intermediate in the production of renewable transportation fuels. To evaluate the stability of the bio-oils from the barley streams, a portion of the ESP bio-oils was stored at 90 °C and sampled for GPC analysis after 8 and 24 h. These conditions were used to mimic room temperature storage for 3−6 months and 9−12 months, respectively.[19] The molecular weight distributions of the bio-oils before and after the aging period are presented in Figure 2. After 8 h at 90 °C, the M_n of the bio-oil from barley straw increased to 335 and the M_w to 446, and M_n further increased to 362 and M_w to 609 after 24 h of storage. For the bio-oil from hulls, the increase in M_n and M_w was to 329 and 518 after 8 h and 341 and 626 after 24 h. These molecular weight increases are similar to those reported in aging studies with bio-oil from woods, grasses, and wheat straw.[20] In neither case was a change in the homogeneity nor the solubility of the bio-oil samples in THF observed. The DDGS bio-oil was the most unstable despite its lower concentration of organic acids and its more neutral pH. This may be a result of cross-linking of the protein fragments present in the bio-oil through reactions of two or more protein-derived amine groups with multifunctional oxygenated compounds present in the bio-oil.[23] After 8 h of storage at 90 °C, its M_n increased to 376 and its M_w to 565, and after 24 h at 90 °C, the bio-oil had polymerized to the point that it was no longer soluble in THF. Therefore, while bio-oil from DDGS contained the most energy and may be less corrosive because of its neutral pH, its utility may be limited by polymerization during storage.

Coproduct Characterization and Energy Balance. The major coproduct from bio-oil production by fast pyrolysis is biocharcoal. Biocharcoal has the potential to be a valuable soil amender which also sequesters carbon. It can also be combusted as a renewable solid fuel. The composition of the biocharcoals produced from fast pyrolysis of the barley biomass streams only significantly differed from each other in ash content. The biocharcoal from the barley straw contained the least ash (20%) and therefore had the highest raw energy content "as is", but on an ash-free basis, C/O ratios were similar for all of the biochars (Table 4). The biocharcoals had energy contents of 24, 18, and 21 MJ/kg for straw, hulls, and DDGS, respectively. The other coproduct of fast pyrolysis is NCG (syngas). The NCG produced from the straw had the best fuel quality, containing the least amount of noncombustible CO_2 (Table 5). The NCG produced by the pyrolysis of barley biomass streams could provide 11−20% of the required energy to run the pyrolysis system, if recycled and combusted. As a result, the remaining energy required to operate a self-sufficient pyrolysis process from any of the feedstocks must come from the combustion of some of the biocharcoal or bio-oil. Figure 3 presents the system's percent energy recovery based on the inputs (biomass and electricity use for heating) and products. Overall, the bio-oil contained 60−70% of the input energy, biochar 13−17%, and NCG 2−3%, meaning the total process energy recovery efficiency was 80−90%.

Conclusions

Biomass streams resulting from barley harvesting, dehulling, and fermentation include straw, hulls, and DDGS. These biomass streams will become more available for the

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production of advanced biofuels as the use of barley as a cover crop and as a fuel ethanol feedstock increase. Fast pyrolysis is a method that could efficiently utilize each of these biomass streams to produce additional biofuel. We demonstrated that pyrolysis of these biomass streams can result in the production of energy-dense bio-oil in ~70 wt % yield. While the bio-oil produced from barley straw and hulls had properties and compositions similar to those of pyrolysis oils reported for other typical lignocellulosic biomass (i.e., wood, herbaceous grasses), the pyrolysis of barley DDGS produced bio-oil that was significantly different due to the composition of the feedstock, including its high protein content. The bio-oils from straw and hulls were acidic and exhibited some instability, as measured by M_w increases over time, but they did not exhibit a change in homogeneity or solubility. These bio-oils had dry-basis energy contents of 24 MJ/kg, ~60% that of petroleum. Bio-oil from DDGS had a very high energy content, ~80% that of petroleum (dry basis) and was nearly pH-neutral. However, utilization of this bio-oil may be more difficult because it was less stable over time and became more heterogeneous and viscous than the bio-oils produced from straw or hulls.

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