Complete Utilization of Spent Coffee Grounds To Produce Biodiesel, Bio-Oil, and Biochar

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Ⓢ *Supporting Information*

ABSTRACT: This study presents the complete utilization of spent coffee grounds to produce biodiesel, bio-oil, and biochar. Lipids extracted from spent grounds were converted to biodiesel. The neat biodiesel and blended (B5 and B20) fuel properties were evaluated against ASTM and EN standards. Although neat biodiesel displayed high viscosity, moisture, sulfur, and poor oxidative stability, B5 and B20 met ASTM blend specifications. Slow pyrolysis of defatted coffee grounds was performed to generate bio-oil and biochar as valuable co-products. The effect of feedstock defatting was assessed through bio-oil analyses including elemental and functional group composition, compound identification, and molecular weight and boiling point distributions. Feedstock defatting reduced pyrolysis bio-oil yields, energy density, and aliphatic functionality, while increasing the number of low-boiling oxygenates. The high bio-oil heteroatom content will likely require upgrading. Additionally, biochar derived from spent and defatted grounds were analyzed for their physicochemical properties. Both biochars displayed similar surface area and elemental constituents. Application of biochar with fertilizer enhanced sorghum−sudangrass yields over 2-fold, indicating the potential of biochar as a soil amendment.

KEYWORDS: *Coffee grounds, Coffee oil, Biodiesel, Bio-oil, Biochar, Pyrolysis*
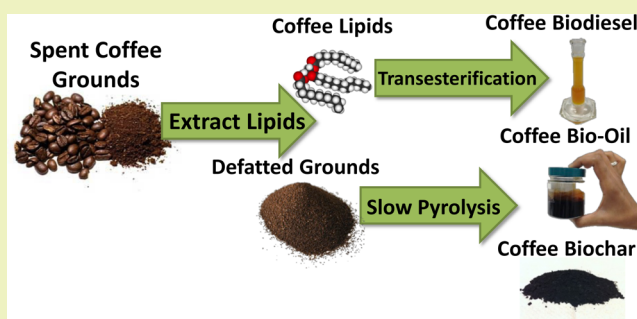
INTRODUCTION

Coffee is one of the largest agricultural commodities traded worldwide, with annual production at ~8 billion kg per year.[1] Commercial coffee beverage production generates substantial quantities of spent grounds that present a significant waste disposal challenge. Spent coffee grounds are problematic for disposal due to the high oxygen demand during decomposition and potential release of residual caffeine, tannin, and polyphenol contaminants to the environment.[2] Valorization of spent coffee grounds is a promising alternative to reclaim energy[3] and produce biodiesel, bio-oil, and biochar while generating stabilized solids for carbon storage and soil amendment.

Spent coffee grounds are attractive for biodiesel production due to their high lipid content, which is ~15% by dry weight.[4] The use of spent grounds avoids competition with food resources compared to conventional lipid feedstocks, such as soybeans and rapeseed.[5] Coffee biodiesel can be used neat or blended with petroleum diesel at various levels (e.g., B5, B20) for enhanced engine compatibility.[6] While the production of coffee biodiesel has been examined,[7] to our knowledge, studies have yet to explore fuel properties of biodiesel blends with petroleum diesel and its adherence to fuel standards.

The remaining defatted coffee grounds also present a potential opportunity for co-product recovery via slow pyrolysis. Slow pyrolysis concentrates biomass carbon and reduces the solid waste disposal footprint by producing bio-oil and biochar. Slow pyrolysis usually occurs between 400 and 600 °C, with a relatively moderate heat-up rate (0.1−1 °C/sec) compared to fast (10−200 °C/min) or flash pyrolysis (>1000 °C/min).[8] Slow pyrolysis bio-oils have a high energy density on a moisture-free basis (20−37 MJ/kg)[9−11] that approaches petroleum crude oils (41−48 MJ/kg).[12] Furthermore, bio-oil condenses energy into a liquid form, allowing for distributed processing and reduced transportation costs.[13] In addition, biochar has a high energy density ranging from 30 to 34 MJ/kg and can be used as a solid fuel.[10,14] However, the use of biochar as a soil amendment and carbon storage medium has also garnered significant interest.[15] When added to soil, biochar can

improve the soil quality by adjusting soil pH, improving soil moisture retention, enhancing the microbial population, and increasing nutrient-use efficiency.[16] Biochar is also resistant to decomposition and mineralization, locking carbon in a stable form.[15] However, to our knowledge, studies have yet to examine the (i) slow pyrolysis of spent coffee grounds, (ii) influence of defatting on bio-oil properties, or (iii) use of coffee biochar as a soil amendment.

The objective of this study is to demonstrate the complete utilization of spent coffee grounds for energy recovery and soil amelioration by extracting residual lipids for biodiesel production and converting defatted grounds into bio-oil and biochar via slow pyrolysis (Figure 1). In this work, spent coffee
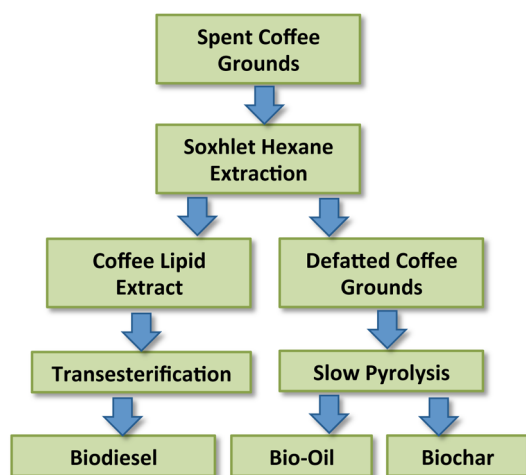
Figure 1. Processing scheme for complete utilization of spent coffee grounds.

grounds were collected from local coffee shops. Lipids were extracted and converted into biodiesel to determine their neat and blended (B5 and B20) fuel properties against ASTM and EN standards. Slow pyrolysis of defatted grounds was then performed to produce bio-oil and biochar. The effect of feedstock defatting on pyrolysis was examined, and bio-oil analyses included elemental and functional group composition, compound identification, and molecular weight and boiling-point distributions. Additionally, biochars were analyzed for their elemental composition, surface area, and application as a soil amendment for sorghum−sudangrass cultivation.

■ MATERIALS AND METHODS

Spent and Defatted Coffee Grounds. Spent coffee grounds (e.g., grounds generated after brewing) were collected from local Starbuck's coffee shops with an average moisture content of 60%, consistent with past studies.[7] Spent grounds were spread into a thin layer and dried at 105 °C overnight to remove residual moisture. Lipids were then extracted using hexane in a Soxhlet apparatus. The extraction proceeded until the refluxing solvent became clear (∼8 h). Hexane was removed from the extract by rotary evaporation under reduced pressure until no further changes in sample weight were observed.

Spent and defatted coffee grounds were analyzed for their nutritional and elemental composition. Forage analysis was performed by Midwest Laboratories (Omaha, NE) to determine crude protein, neutral detergent fiber (hemicellulose, cellulose, and lignin), acid detergent fiber (cellulose and lignin), and ash content. Nutrient analysis was also performed by Midwest laboratories to determine major, secondary, and micronutrients. Elemental analysis of spent and defatted coffee grounds was conducted at the University of Illinois

Microanalysis Laboratory (Urbana, IL). Samples were processed for total carbon/hydrogen/nitrogen using an Exeter analytical CE-440 elemental analyzer. Oxygen was calculated by mass balance closure. Higher heating values (HHV) of the coffee grounds were measured using a Parr 1281 isoperibol oxygen bomb calorimeter. Standard 1 g pellets of benzoic acid were used for calibration. Acid corrections were based on sodium carbonate titration with no correction for sulfur.

Lipids extracted from spent coffee grounds were analyzed for their fatty acid profile. Fatty acids were esterified prior to analysis.[17] Spent coffee oil methyl esters were separated using a HP 5890 Series II GC equipped with a FID detector and a Supelco SP-2380 column (30 m × 0.25 mm i.d., 0.20 μm film thickness). Helium (1 mL/min) was used as the carrier gas. The oven temperature increased from 170 to 190 °C at 4 °C/min, followed by an increase to 265 °C at 30 °C/min, with a final hold time of 2.5 min. The injector volume was set to 1 μL with the injector and detector temperature set at 250 °C. Peaks were identified (triplicates, means reported) by comparison to reference standards.

Coffee Biodiesel and Biodiesel Blends. Coffee lipids were pretreated prior to base-catalyzed transesterification to reduce their acid value (AV). Acid-catalyzed pretreatment was accomplished in a 1 L three-necked round-bottomed flask connected to a reflux condenser and a mechanical magnetic stirrer set to 1200 rpm. Initially, coffee oil and methanol (35 vol %) were added to the flask, followed by dropwise addition of sulfuric acid (conc., 1.0 vol %). The contents were heated at reflux for 4 h. Upon cooling to room temperature, the phases were separated. The oil phase was washed with distilled water until a neutral pH was achieved, followed by rotary evaporation (20 mbar; 30 °C) to remove residual methanol.

Acid-pretreated coffee lipids were transesterified using conventional alkaline-catalyzed methanolysis to prepare coffee biodiesel. Methanolysis was conducted in a 1 L three-necked round-bottomed flask connected to a reflux condenser and a mechanical magnetic stirrer set at 1200 rpm. Initially, the extracted lipids and methanol (1:6 molar ratio) were added and heated to 60 °C, followed by the addition of sodium methoxide catalyst (0.50 wt % with respect to lipids). After reacting for 1 h, the mixture was equilibrated to room temperature, and the lower glycerol phase was removed by gravity separation (>2 h settling time). Methanol was removed from the ester phase by rotary evaporation at reduced pressure. Spent coffee biodiesel was washed with distilled water until a neutral pH was obtained and then was dried with $MgSO_4$ to yield neat biodiesel. Neat biodiesel was also blended with ultralow sulfur petroleum diesel (ULSD) at 5% and 20% volume to produce B5 and B20 blends, respectively. Certification grade ULSD was donated by a major petroleum company that wishes to remain anonymous. Characterization results were compared for ULSD, extracted coffee lipids, coffee biodiesel, soy biodiesel,[18] and respective biodiesel blends.

Coffee Biodiesel Characterization. Fuel properties of neat and blended coffee biodiesels were measured in triplicate following AOCS, ASTM, and CEN standard test methods using instrumentation described previously.[6,19,20] Standard test methods included cloud point (CP, °C), ASTM D5773; pour point (PP, °C), ASTM D5949; lubricity (mm), ASTM D6079; ASTM D4052; kinematic viscosity (mm²/s), ASTM D445; specific gravity (SG), AOCS Cc 10c-95; induction period (IP, h), EN 15751; acid value (AV, mg KOH/g), AOCS Cd 3d-63; derived cetane number (DCN), ASTM D6890; free and total glycerol (single determinations), ASTM D6584; moisture content (ppm), ASTM D6304; gross heat of combustion (higher heating value, HHV, MJ/kg), ASTM D4809; sulfur (S, ppm), ASTM D5453; and phosphorus (P, mass %), ASTM D4951.

Slow Pyrolysis. Slow pyrolysis was conducted using a Thermolyne 79400 tube furnace as described in detail previously.[11] Briefly, conversions were conducted using 100 g of dry feedstock heated to 450 °C at a rate of 50 °C/min. The retention time was 2 h with a nitrogen sweep gas. An ice-chilled collection vessel condensed volatile products. The remaining solids in the tube furnace were massed and hereon referred to as biochar. Condensed liquids were fractionated using dichloromethane (DCM) to separate bio-oil (DCM-soluble phase) and aqueous-phase organics. Residual particulates (<1% of

initial biomass) in the DCM and water phases were removed using a Millipore pressurized filtration assembly and Satorious 0.45 μm cellulose membrane. The mass of the aqueous phase was measured gravimetrically after fractionation. DCM was removed from the bio-oil phase by rotary evaporation under reduced pressure. The product phase mass balance was calculated as a fraction of the initial dry feedstock mass, with the gas-phase yield determined by closure.

Bio-Oil Characterization. Bio-oils were characterized in detail using methods described previously[21] to determine their bulk and physicochemical properties. Bio-oil elemental compositions and sulfur contents were measured using the Exeter elemental analyzer and PerkinElmer ICP-OES described above. Low-boiling constituents were identified by gas chromatography–mass spectroscopy (GC-MS). Chemical functional groups were profiled using attenuated total reflectance-Fourier Transform infrared (ATR-FTIR) and ¹H-nuclear magnetic resonance spectroscopy (¹H NMR), and bio-oil molecular weight and boiling point distributions were analyzed using size exclusion chromatography (SEC) and simulated distillation (Sim-Dist), respectively. Bio-oil HHVs were measured using the Parr bomb calorimeter described above.

Biochar Characterization and Soil Application. Biochars were evaluated to determine their bulk properties, nutrient profile, and performance as a soil amendment. Biochar elemental compositions, nutrient profile, and HHVs were determined using methods described above. Ash content was determined gravimetrically after heating a known amount of sample at 800 °C for 1.5 h with an air purge flow rate of 450 mL/min. Moisture was determined gravimetrically after heating a known amount of sample at 140 °C for 1.5 h with a nitrogen purge flow rate of 70 mL/min. Single point BET surface areas were determined using nitrogen adsorption and desorption isotherms at −196 °C with a Monosorb (Quantachrome Inc.) N_2 adsorption analyzer.[22]

The performance of biochar as a soil amendment for sorghum–sundangrass cultivation was evaluated in a temperature-controlled greenhouse (20–25 °C). The greenhouse experiments were managed according to standard greenhouse growing practices.[23,24] Sorghum–sundangrass was selected due to its rapid growth and dual utilization as a forage crop and bioenergy feedstock.[25] Ten sorghum–sundangrass seeds were planted in 1500 mL containers using 750 g of organic top soil obtained from Peat Corp and 750 g of vermiculite obtained from Sun Gro Horticulture. Spent coffee grounds, defatted grounds, and biochar derived from these feedstocks were mixed as soil additives at 2 wt %. Cultivation experiments were also conducted without coffee additives as a control. The influence of soil additive on biomass productivity was tested with and without fertilizer application using 40 mg of Scotts' General Purpose water-soluble fertilizer (NH_4NO_3). Three replicates were employed for each treatment. During growth, external lighting was not used, and watering was scheduled twice per week. Seedlings were cultivated for an average of 40 days, after which the plants were harvested, washed, dried, and weighed to determine the biomass growth. Because of the small quantities of biomass collected from each pot, biomass samples from three triplicate pots were weighed collectively to determine biomass productivity yields for each treatment.

■ RESULTS AND DISCUSSION

Spent and Defatted Coffee Grounds. The spent coffee and defatted coffee grounds used in this study were primarily composed of neutral detergent fiber (NDF) (45.2% spent; 58.9% defatted), representative of hemicellulose, cellulose, and lignin (Table 1). Acid detergent fiber (ADF), representative of cellulose and lignin, was also significant (29.8% spent; 40.2% defatted), indicating that a large fraction was comprised of hemicellulose. The level of protein was comparable for both feedstocks (15.4% spent; 18.2% defatted), which distinguishes coffee grounds from woody biomass that contains negligible protein and over 80% NDF.[9] Spent coffee grounds contained 16.2% lipid. By contrast, very small quantities (0.3%) were

Table 1. Initial Moisture Content (wt %), Nutritional Analysis, Fatty Acid Profile, Elemental Composition, And Higher Heating Value (HHV) of Spent and Defatted Grounds

collected grounds initial moisture (wt %)	50−60	
property	spent coffee grounds	defatted coffee grounds
nutritional analysis		
crude protein	15.4	18.2
crude lipid	16.2	0.3
NDF	45.2	58.9
ADF	29.8	40.2
ash	1.8 (0.17)	2.4 (0.12)
fatty acid profile		
16:0	33.9	−
18:0	7.3	−
18:1	8.3	−
18:2	45.0	−
18:3	1.5	−
20:0	2.5	−
20:1	0.4	−
22:0	0.6	−
elemental analysis		
C	56.1	51.8
H	7.2	6.3
N	2.4	2.8
O	34.0	38.8
S	0.14	0.17
P	0.18	0.17
HHV (MJ/kg)	23.4	20.1

detected in the defatted grounds. The nutritional composition of the spent coffee grounds was comparable to previous reports of grounds collected from various sources.[2] The fatty acid profile of the extracted lipids revealed a high percentage of polyunsaturated fatty acids (46.5%), consisting predominantly of linoleic acid (45.0%) (Table 1). The high percentage of polyunsaturated fatty acids was consistent with previous studies for coffee oil.[26] Saturated fatty acids were also detected, with palmitic acid being the most prevalent (34.9%).

Elemental analysis of the coffee grounds revealed a higher oxygen content for the defatted feedstock (34.0% spent; 38.8% defatted). The oxygen content resulted in a lower HHV of 20.1 MJ/kg for the defatted grounds, compared to 23.4 MJ/kg for the spent grounds, as measured by calorimetry. The residual energy content of defatted coffee grounds is comparable to woody biomass (19−21 MJ/kg),[27] making it a suitable feedstock for thermochemical conversion or direct combustion. However, the coffee protein fraction resulted in a N content of 2.4% for spent grounds and 2.8% for defatted grounds, likely resulting in high NO_x emissions with direct combustion. Ideally, nitrogen would be recovered during biomass valorization for fertilizer application. The S content of the spent and defatted grounds was minimal (0.14−0.17%), which is advantageous for thermochemical conversion to produce bio-oil.

Coffee Biodiesel. Neat lipids extracted from spent coffee grounds displayed a prohibitively high AV (11.27 mg KOH g^{-1} initial) for traditional homogeneous based-catalyzed transesterification, requiring acid-catalyzed pretreatment for reduction. The acid-pretreated lipids produced coffee biodiesel in

Table 2. Fuel Standards and Lipid and Biodiesel Fuel Properties for Refined, Bleached, and Deodorized (RBD) Soy Biodiesel, Spent Coffee Lipids, and Coffee Biodiesel[a]

fuel property	ASTM D6751	EN 14214	soy biodiesel[18]	spent coffee lipids initial	coffee biodiesel
cloud point (°C)	report	–	0	12.2 (0.1)	13.1 (0.3)
pour point (°C)	–	–	−3	7.0 (0.0)	13.0 (0.0)
lubricity at 60 °C (μm)	–	–	135	180 (2)	175 (4)
kin. visc. 40 °C (mm²/s)	1.9–6.0	3.5–5.0	4.12	49.64 (0.07)	5.19 (0.00)
sp. gravity	–	–	0.8823	0.9411	0.8920
Rancimat ind. 110 °C (h)	3.0 min	6.0 min	5.0	8.4 (0.4)	0.2 (0.0)
acid value (mg KOH/g)	0.50 max	0.50 max	0.01	11.27 (0.14)	0.11 (0.01)
cetane number	47 min	51 min	54.1	–	60.1 (1.1)
free glycerol (mass %)	0.020 max	0.020 max	0.004	–	0.005
total glycerol (mass %)	0.240 max	0.250 max	0.071	–	0.098
moisture content (ppm)	0.050[b] vol % max	500[c] ppm	202 (6)	330 (8)	632 (2)
P/S (ppm)	15/10	10/4	<1/<1	0.2/60.1	0.0/35.9
HHV (MJ/kg)	–	–	39.9	–	39.6

[a]Values in parentheses indicate standard deviations from triplicate measurements. [b]Free water. [c]Dissolved water.

Table 3. Fuel Standards and Biodiesel Blend Fuel Properties for B5 and B20 Coffee and Soy Biodiesel[a]

| fuel property	ASTM D975	ASTM D7467	ULSD	coffee B5	soy B5[18]	coffee B20	soy B20[18]
vol % biodiesel	0–5	6–20	0	5	5	20	20
cloud point (°C)	report	–	−14.9 (0.2)	−13.2 (0.2)	−16	−4.7 (0.4)	−12
pour point (°C)	–	–	−24.3 (0.6)	−22.7 (0.6)	−22	−11.7 (0.6)	−17
lubricity at 60 °C (μm)	520 max	520 max	493 (10)	186 (14)	198	141 (2)	143
kin. visc. 40 °C (mm²/s)	1.9–4.1	1.9–4.1	2.23 (0.00)	2.40 (0.01)	2.37	2.75 (0.01)	2.54
sp. gravity	–	–	0.8483	0.8501	0.8480	0.8564	0.8540
Rancimat ind. 110 °C (h)	–	6.0 min	>24	13.2 (0.6)	>24	5.2 (0.2)	17.1
acid value (mg KOH/g)	–	0.3 max	0.05 (0.04)	0.17 (0.04)	0.01	0.16 (0.01)	0.01
cetane number	40 min	40 min	42.5	50.5	43.8	51.9	46.5
moisture content (ppm)	–	–	17 (1)	43 (1)	27 (3)	124 (3)	56 (6)
P/S (ppm)	15/–	15/–	ND/9.2	0/9.4	ND/8.6	0/14.1	ND/7.2
HHV (MJ/kg)	–	–	44.2	44.8	44.7	43.9	40.0

[a]Values in parentheses indicate standard deviations from triplicate measurements.

high yield (96 wt %), with a low biodiesel AV (0.11 mg KOH/g), as shown in Table 2. The energy density of the coffee biodiesel (39.6 MJ/kg) was comparable to biodiesel derived from refined, bleached, and deodorized soybean oil (39.9 MJ/kg) and other plant lipid-derived biodiesels.[28] However, several coffee biodiesel properties were outside of ASTM D6751 or EN 14214 specifications, including the kinematic viscosity, oxidative stability (indicated by Rancimat IP), moisture, and S content. Because of higher amounts of saturated fatty acids, the CP and PP of the coffee biodiesel were also elevated (13.1 and 13.0 °C, respectively) compared to soy biodiesel (0 °C and −3 °C, respectively), indicating poor cold weather performance.

The high kinematic viscosity and S content may be due to the large percentage of saturated methyl ester chains and polar compounds, respectively,[29] while the high moisture content may be attributable to carry over during the water washing step. During transesterification, natural antioxidants may also be lost, resulting in poor oxidative stability compared to neat lipids.[29] Refining, bleaching, and deodorizing extracted coffee lipids prior to conversion may help improve the final biodiesel viscosity, cold flow properties, and S content by removing waxes, sterols, heteroatom-containing compounds, and free fatty acids.[30,31] Other fuel properties of the coffee biodiesel (e.g., AV, cetane number, free and total glycerol) were within ASTM and EN specifications.

Blending of coffee biodiesel with ULSD greatly enhanced its fuel properties, providing a final product meeting ASTM D975 and D7467 specifications, as shown in Table 3. The kinematic viscosity (2.4 mm²/s B5; 2.75 mm²/s B20), moisture content (43 ppm B5; 124 ppm B20), and S content (8.6 ppm B5, 14.1 ppm B20) were significantly improved through blending, which may lead to improved fuel injector performance, fuel flowability, and combustion byproducts.[5] Likewise, the oxidation stability was significantly extended, resulting in a prolonged Rancimat induction period (13.2 h B5; 5.2 h B20). The cold weather properties also benefited, leading to reduced CP and PP values for B5 (−13.2 °C, −22.7 °C) and B20 (−4.7 °C, −11.7 °C). Overall, blending coffee biodiesel with ULSD produced a high quality fuel that met ASTM biodiesel blend specifications.

Slow Pyrolysis Mass Balance. Slow pyrolysis of defatted coffee grounds resulted in a bio-oil yield of 13.7%, which was roughly half yield of bio-oil obtained from spent coffee grounds (27.2%), as shown in Figure 2. The lower bio-oil yield from defatted grounds is likely due lipid extraction, consistent with previous findings for raw and defatted microalgae.[11] Lipids are known to rapidly breakdown during pyrolysis into bio-oil organics, which include alkanes, fatty acids, esters, ketones, and acrolein.[32] In contrast, the pyrolysis aqueous-phase yield from defatted grounds was much higher (33.3%) compared to spent grounds (23.8%). The higher yield of aqueous-phase constituents may be due to the elevated content of cellulose
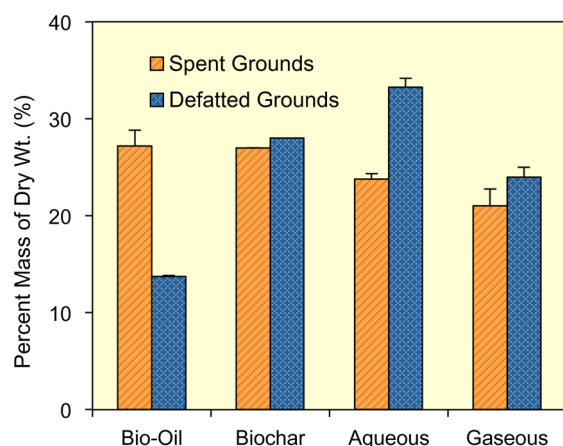
Figure 2. Mass balance yield for the product phases derived from the slow pyrolysis of spent coffee grounds and defatted spent coffee grounds.

and hemicellulose after lipid extraction because these components can degrade into water-soluble organics.[10] Energy recovery from pyrolysis aqueous-phase organics is of interest for a potential source of hydrogen, alkanes, and polyols.[33] The biochar solids yield (27.0−28.0%) and gas phase yield (21.0−24.0%) were comparable for spent and defatted grounds, with biochar yields similar to previous studies for spent coffee grounds.[14]

Bio-Oil Properties. Elemental Composition and HHV. Bio-oil (moisture-free basis) derived from spent and defatted coffee grounds increased the carbon density and reduced the oxygen content compared to the original feedstocks, as shown in Table 4. The elevated carbon density resulted in high bio-oil energy HHVs (32.3 MJ/kg spent; 27.0 MJ/kg defatted). Although lipid extraction reduced the energy density of pyrolysis bio-oil, the HHV was still comparable to other renewable fuels, such as ethanol (28.9 MJ/kg). The oxygen content of the both feedstocks (34.3% spent feedstock; 39.1% defatted feedstock) was greatly reduced in the bio-oil (13.4% spent bio-oil; 16.4% defatted bio-oil). In contrast, a significant portion of the feedstock nitrogen content was carried over into the pyrolysis bio-oil phase resulting in moderate bio-oil N contents (2.6% spent; 4.3% defatted). The coffee bio-oil N content was comparable to fast pyrolysis studies with spent coffee grounds (3.06%);[34] however, these values are much higher compared to bio-oils derived from woody biomass, which typically contain less than 1% N content due to the low feedstock protein content.[9] Defatting resulted in a bio-oil with lower C and H and higher N and O, which is likely due to the removal of the aliphatic lipid fraction that shifts the overall biomass composition, as shown in Table 1.

Overall, the total bio-oil heteroatom content (16.2% spent bio-oil; 21.1% defatted bio-oil) was greatly reduced compared to the feedstock (36.7% spent feedstock; 41.9% defatted feedstock) and consistent with other slow pyrolysis bio-oils

produced at similar temperatures from algae (16.8−19.9%)[35] and cherry seeds (23.8−24.4%).[10] However, the high heteroatom content greatly distinguishes slow pyrolysis bio-oils from conventional petroleum crude oils, which typically contain <4% total heteroatoms.[12] Furthermore, removal of bio-oil N is problematic and remains a challenge because it can result in fouling of acidic sites during catalytic upgrading.[36,37]

Identification of Volatile and Semivolatile Constituents. The major volatile constituents of the coffee bio-oil constituents were identified by GC-MS, as indicated by >1% of the total ion chromatogram area (TIC), and categorized, as shown in Table 5. A full listing of major compounds and representative chromatogram are reported in Table S1 and Figure S1 of the Supporting Information. Analysis of mass spectra revealed that both coffee-derived bio-oils contained a high percentage of oxygenated compounds (32.8−48.3%), comprised primarily of phenolic and methylphenolic compounds. The high percentage of phenolic compounds is consistent with the high ADF (lignin and cellulose) content of the coffee ground feedstocks, similar to observations with wood-derived bio-oils.[9] Varying classes of nitrogenated compounds, including caffeine, indole, amine, and nitrile-derivatives, were also observed, which is consistent with the protein content of the feedstock. As expected, the bio-oil derived from spent coffee grounds contained more hydrocarbon products compared to the defatted coffee bio-oil due to the removal of lipids. Lipids are known to readily decompose into hydrocarbons during pyrolysis;[38] however, they may have greater economic value when used for biodiesel. Hydrocarbon compounds were also observed in the bio-oil derived from defatted coffee, which may be due to heteroatom removal from other biomass fractions (e.g., proteins) during conversion.[11,39]

Functional Group Analysis. Defatting spent coffee grounds prior to pyrolysis influenced the bio-oil functional groups observed by ATR-FTIR (Figure 3a) and ^{1}H NMR (Figure 3b). References for the ATR-FTIR bio-oil functional peak assignments were based on previous pyrolysis studies.[38,40] Bio-oils derived from defatted coffee grounds contained more prevalent functional peaks at 1650 cm^{-1} and 1600 cm^{-1} compared to bio-oil derived from spent coffee grounds, possibly due to increased N−H bending or C=O stretch from amide, ketone, and carboxylic groups associated with the higher feedstock protein content. Other peaks consistent with bio-oil derived from a high protein feedstock were observed in both spectra, including C−N stretch (1335−1020 cm^{-1}) and N−H wag (910−665 cm^{-1}).[11,40] Aliphatic peaks, consistent with the high bio-oil energy density, were prevalent as expected, and included C−H stretch (3000−2800 cm^{-1}) and C−H bending (1465 cm^{-1}, 1375 cm^{-1}). A broad peak from 3400 to 3000 cm^{-1} and multiple sharp peaks from 1300 to 1100 cm^{-1} were also observed, likely due to the C−O stretch and O−H stretch from phenolic, carboxylic, or alcohol moieties, consistent with compounds identified by GC-MS.
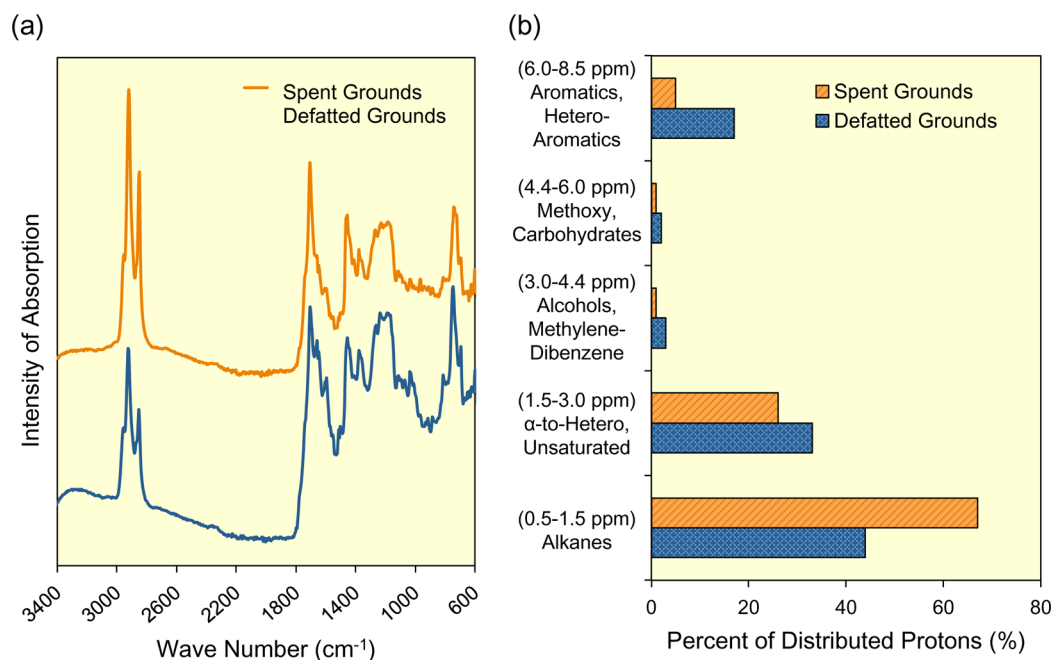
Table 4. Elemental Analysis, Higher Heating Values (HHV), and Molecular Weight Parameters of Slow Pyrolysis Bio-Oils Derived from Spent and Defatted Coffee Grounds[a]

bio-oil feedstock	C (%)	H (%)	N (%)	O (%)	S (%)	HHV (MJ/kg)	M_n	M_w	PDI
spent grounds	74.0 (0.9)	9.8 (0.2)	2.6 (0.1)	13.4 (0.9)	0.17	32.3	596	2357	3.96
defatted grounds	70.9 (0.5)	8.0 (0.0)	4.3 (0.0)	16.4 (0.5)	0.39	27.0	651	2670	4.10

[a]Values in parentheses indicate standard deviations from triplicate measurements.

Table 5. Percent of Total Ion Chromatogram (TIC) of Chemical Constituents Identified by Class Using GC-MS for Slow Pyrolysis Bio-Oils Derived from Spent and Defatted Coffee Grounds

bio-oil feedstock	straight and branched hydrocarbons	cyclic hydrocarbons	straight and branched oxygenates	cyclic oxygenates	straight and branched nitrogenates	cyclic nitrogenates	N and O straight and branched	N and O cyclic
spent coffee grounds	10.0	4.3	12.8	17.0	1.9	ND	1.9	1.1
defatted coffee grounds	3.2	3.2	2.5	43.4	ND	1.3	ND	2.4

Figure 3. FTIR-ATR spectra (a) and ^1H NMR spectral distribution of functional groups (b) of bio-oil derived from spent and defatted coffee grounds.

The ^1H NMR spectra (raw spectra shown in Figure S2, Supporting Information) revealed further differences in the functionality of spent and defatted coffee ground bio-oils, with spectra area integration assignments (Figure 3) based on previous studies.[41] Bio-oil derived from spent grounds contained a higher percentage of aliphatic protons (67%) compared to the bio-oil derived from defatted coffee grounds (44%), consistent with the higher lipid content and hydrocarbon products identified by GC-MS. Both bio-oils displayed comparable integration regions for protons alpha to a heteroatom group or unsaturated bond (26% spent, 33% defatted), likely due to the high heteroatom content determined from elemental analysis. Lastly, bio-oil derived from defatted coffee grounds displayed a higher aromatic/heteroaromatic content (17%), consistent with the larger percentage of cyclic structures containing oxygen and nitrogen functional groups identified by GC-MS.

Molecular Weight and Boiling Point Distribution. Bio-oil molecular weight and boiling point distributions were profiled to determine the influence of feedstock defatting on the physico-chemical characteristics of bio-oils. The number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI) were used to characterize the molecular weight distribution of the bio-oils. These parameters were calculated based on component molecular weights (M_i) determined from the retention time

calibration curve and signal intensities (N_i) in size exclusion chromatography data

$$M_n = \frac{\sum M_i N_i}{\sum N_i}$$

$$M_w = \frac{\sum M_i^2 N_i}{\sum M_i N_i}$$

The polydispersity index (PDI) was then calculated according to

$$PDI = \frac{M_w}{M_n}$$

As shown in Table 4, bio-oil derived from spent coffee grounds displayed a comparable number average MW (MW_n 596 Da) and weight average molecular weight (MW_w 2357 Da) compared to bio-oil derived from defatted coffee grounds (MW_n 651 Da; MW_n 2670 Da). Both bio-oils had similar polydispersity indices, (3.96−4.10), consistent with the diverse range of decomposition products generated during pyrolysis. However, analysis of the MW distribution profile (Figure S3, Supporting Information) revealed a prominent peak near 700 Da for the bio-oil derived from spent coffee grounds, which may be due to incomplete lipid decomposition products (i.e., acylglycerides). A similar trend was observed in the MW distribution of bio-oils derived from raw and defatted

microalgae.[11] Overall, the coffee-derived bio-oil MW_n values were comparable to bio-oils derived from woody biomass (580−590 Da)[9] but much higher compared to petroleum crude oils that have a MW_n of ∼250 Da.[12]

Characterization of the bio-oil boiling point distribution, as shown in Figure 4, further highlighted the influence of
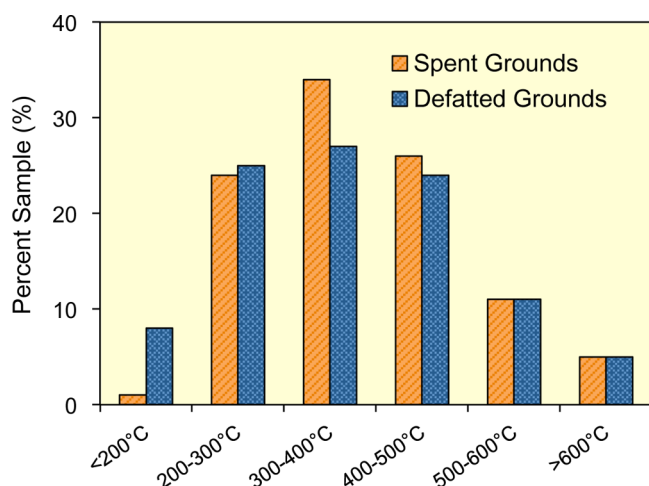
Figure 4. Sim-Dist boiling point distribution of bio-oils derived from spent and defatted coffee grounds.

feedstock defatting and the need for bio-oil upgrading. Both coffee-derived bio-oils contained a large percentage of high boiling compounds (40−41% >400 °C), likely due to the presence of oligomer compounds and polar functional groups. More than half of the boiling point distribution fell within 200−400 °C, the equivalent petrol distillation range of kerosene, diesel, and fuel oil.[12] Bio-oil derived from spent coffee grounds contained the highest percentage of compounds with boiling points between 300 and 400 °C (34%), likely due to the prevalence of lipid decomposition products observed by GC-MS. Interestingly, bio-oil derived from defatted grounds had a higher fraction of compounds with boiling points <200 °C (8%), which may be due to the prevalence of phenolic and low molecular weight oxygenated compounds identified by GC-MS. Both bio-oils contained comparable total distillables (88−89% bp <538 °C), which is similar to the percentage for petroleum crude oil.[12] However, the coffee bio-oils' high heteroatom content, molecular weight distribution, and boiling point distribution will likely require catalytic upgrading to allow for compatibility with conventional refining operations.[37]

Biochar Properties and Soil Application. Biochar was another co-product that was evaluated based on its physicochemical properties (Table 6) and performance as a soil amendment (Figure 5). Compared to the energy density of the initial feedstock (20.1−23.4 MJ/kg), coffee-derived biochar displayed an elevated energy density comparable for spent (31.0 MJ/kg) and defatted grounds (28.3 MJ/kg), with the slightly higher value for biochar derived from spent grounds likely due to residual lipid content. Overall, these values were in agreement with past studies for spent coffee ground biochar.[14] The energy density of biochar may allow it to be co-fired as a solid fuel with an energy density comparable to solid fossil fuels.[42] Alternatively, coffee-derived biochar offers potential carbon storage capacity depending on the long-term soil stability with 27.6−28.6% of the initial biomass carbon being retained.

Table 6. Solid Sample Characterization of Initial Feedstock and Biochar Samples Derived from Spent Coffee Grounds and Defatted Spent Coffee Grounds[a]

soil additive property	spent coffee grounds	defatted coffee grounds	spent coffee grounds biochar	defatted coffee grounds biochar
moisture (%)	1.3 (0.13)	4.3 (0.20)	1.3 (0.10)	2.0 (0.07)
BET (m^2/g)	0.4	0.5	1.1	1.2
ash (%)	1.8 (0.17)	2.4 (0.12)	3.5 (0.17)	4.1 (0.12)
HHV (MJ/kg)	23.4	20.1	31.0	28.3
C (%)	56.1	51.8	76.2	72.6
H (%)	7.2	6.3	5.6	5.0
N (%)	2.4	2.8	3.9	4.3
S (%)	0.14	0.17	0.05	0.10
P (%)	0.18	0.17	0.48	0.25
K (%)	0.81	0.74	1.94	1.08
Ca (%)	0.20	0.17	0.56	0.54
Mg (%)	0.20	0.22	0.60	0.36
Na (%)	0.07	0.06	0.17	0.13
Zn (ppm)	−	−	51	55
Fe (ppm)	−	73	676	165
Mn (ppm)	42	60	156	79
Cu (ppm)	23	27	105	118
B (ppm)	−	−	31	25

[a]Values in parentheses indicate standard deviations from triplicate measurements.
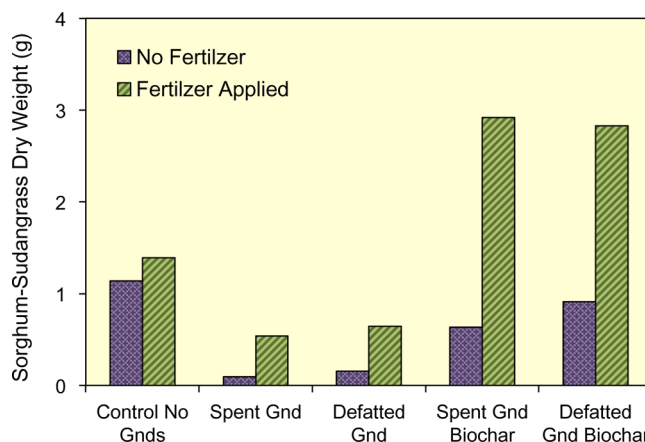
Figure 5. Sorghum−sudangrass biomass productivity with and without fertilizer application using spent coffee grounds, defatted grounds, and their respective biochar derivatives.

Slow pyrolysis of the coffee grounds increased the particle specific surface area, however, not to a significant extent due to the lack of secondary activation treatment. Low-temperature pyrolysis is known to produce biochar with significantly lower surface areas compared to that of activated carbon; however, secondary activation occurs at the expense of reduced carbon storage because significant carbon is lost during activation.[16] The low surface area of coffee ground biochar (1.1−1.2 m^2/g) is comparable to that of biochar derived from other agricultural waste feedstocks, such as corn stover (3.1 m^2/g).[43] However, the ash content of the coffee ground-derived biochar (2.9−3.7%) was much lower compared to that of corn stover biochar (13.1%)[43] due to the elevated stem mineral content of the latter.

Analysis of the major and secondary nutrient profile (S, P, K, Ca, Mg, Na) for spent and defatted coffee grounds revealed comparable results to past reports[14] with trace levels of micronutrients (Zn, Fe, Mn, Cu, B). Overall, slow pyrolysis of the coffee grounds increased the relative weight fraction of nutrients in the biochar, particularly for micronutrients, which may partially account for the increased soil productivity when N is no longer the limiting factor as described below.

The use of coffee-derived biochar as a soil amendment in combination with fertilizer showed a significant enhancement in the biomass yield of sorghum−sundangrass over a 4 -day period, as shown in Figure 5. The addition of biochar in soils resulted in over a 2-fold increase in the biomass dry weight yield (2.92 g w/spent biochar; 2.83 g w/defatted biochar) with fertilizer application compared to control experiments without biochar (1.39 g w/fertilizer). The increase in biomass productivity may be due to multiple factors, including improved nutrient retention in soils, increased soil cation exchange capacity, and adjusted soil pH.[44] Similar gains in biomass productivity (e.g., 2.5-fold increase) have been observed when combining fertilization with biochar derived from greenwaste and papermill waste, indicating that biochar may facilitate fertilization efficiency.[23,24] Without addition of fertilizer, the application of biochar did not increase biomass yields, potentially due to the adsorption of available anions and cations necessary for growth.[24] Similarly, the application of non-pyrolyzed coffee grounds reduced biomass yields compared to the control, potentially due to changes in soil chemistry during their decomposition[45] or the release of bioactive compounds (e.g., caffeine, chlorogenic acids).[46] Residual lipids on the surface of non-defatted grounds may also inhibit moisture transfer, further affecting their performance.[45] However, additional work is needed to determine the primary mechanisms linking coffee biochar physicochemical properties, fertilization efficiency, soil qualities, and crop yields.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Characterization of bio-oil derived from spent and defatted coffee grounds, including a list of major compounds identified by GC-MS and corresponding chromatograms (Table S1 and Figure S1); ^{1}H NMR spectra (Figure S2); and SEC molecular weight distributions (Figure S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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