CHARACTERIZATION OF DEFATTED COTTONSEED MEAL-BASED BIOCHAR AND BIO-OIL

Zhongqi He
USDA-ARS, Southern Regional Research Center
New Orleans, LA
Mingxin Guo
Dept. of Agriculture & Natural Resources
Delaware State University
Dover, DE

To enhance the utilization of agricultural byproducts "green" and value-added raw materials, in this work, we evaluated the feasibility of producing biochar and bio-oil from defatted cottonseed meal (CSM). Complete slow pyrolysis at 300, 400, and 500°C in batch reactors was implemented to convert CSM to biochar and bio-oil. The physicochemical properties of the biochar products were characterized by wet chemistry and advanced spectroscopic techniques. The bio-oil product was separated into an aqueous phase and an oily phase and subsequently characterized using ultrahigh resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. The characterization work increased the knowledge on the chemical and structural composition of cottonseed meal-derived biochar and bio-oil products. The results provide a base for effective utilization of these products in pollutant absorption/immobilization, bio-energy resources or bio-based wood bonding.

Introduction

Although cotton is a non-food crop and provides a major fiber source for textile industry, exploration of the cotton residues for bioenegry and biochars are environmentally and economically feasible for cotton industry (He et al., 2016a; Windeatt et al., 2014). A typical approach for this purpose is pyrolysis (He et al., 2016a; Putun, 2010). While there are several reports from Turkey and India on pyrolysis of defatted cottonseed cake mainly for bio-oil production (Ozbay et al., 2006; Putun et al., 2006; Singh et al., 2014), no pyrolysis of defatted cottonseed meal (CSM, defatted cottonseed product in USA) has been conducted. Therefore, the objectives of this study were to produce biochar and bio-oil by slow pyrolysis of CSM, and 2) to characterize CSM-based biochars and bio-oil with wet chemistry and instrument analysis. The eventual goal of this project is to develop CSM-based biochar products for agricultural pollutant absorption/immobilization and CSM-based bio-oil adhesives for wood bonding.

Materials and Methods

Mill-scale produced CSM was provided by Cotton, Inc. (Cary, NC, USA) and was used as the biomass material for pyrolysis (He et al., 2016b). The CSM was converted to biochar and bio-oil using a custom-made benchtop paralyzer consisting of an oven, a reactor, a condenser, a collector, and a burner (Fig. 1). Approximately 2200 g of the air-dried CSM was packed into the pyrolysis reactor (a 3.78-L iron container with a side vent and movable lid). The reactor was then placed in the oven and heated by the burner (a gel chafing fuel canister). Pyrolysis of CSM started when the temperature inside the reactor reached above 200°C. The resulting pyrolysis vapor passed through the side vent and entered into the condenser, where a room temperature of 22°C was maintained by slowly flowing water. Slow pyrolysis with peak temperature at 300, 350, 400, 450, 500, 550, and 600°C were applied to conversion of cottonseed meal to biochar and bio-oil (He et al., 2016a; Ozbay and Ayrilmis, 2015; Zhang et al., 2015). Whereras biochars for all seven pyrolysis temperatures were collected, only was the bio-oil product at pyrolysis temperature 350°C was collected. The bio-oil was separated into aqueous and oil fractions by a separatory funnel with roughly 57% and 43%, respectively, per the water content (Fig. 2).

The contents of total N and C in each sample were determined using a LECO Truspec dry combustion Carbon/Nitrogen Analyzer. The content of P was analyzed following HNO_3 digestion in the HotBlock Environmental Express block digester and determined by a Spectro CirOs inductively coupled plasma (ICP) spectrometer (Mahwah, NJ, USA). Solid state ^{13}C nuclear magnetic resonance (NMR) spectroscopy were used to characterize biochar samples (He et al., 2015b). Electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS) was used to characterize the bio-oil product.

Fig. 1. Defatted cottonseed meal (left) and custom-made lab-scale slow pyrolysis system (right)

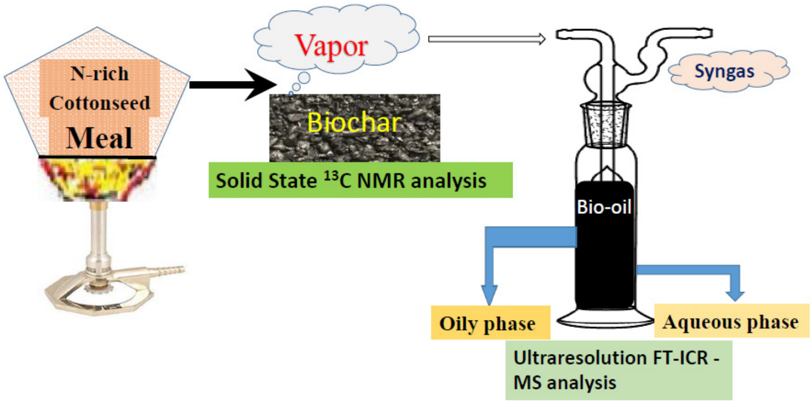

Fig. 2. Pyrolysis products and characterization methods

Results and Discussion

Contents of organic C, total N, and total P in CSM and its biochar products are listed in Table 1. The biochars generated at 300, 350, 400, 450, 500, 550, and 600°C are referred herein to as Char300, Char350, Char400, Char450, Char500, Char550, and Char600, respectively. The mass-based yield of biochar decreased from 53.33% to 32.16% with the increase in pyrolysis temperatures from 300 to 600°C. Recoveries of organic carbon and total N were in the same decreasing trend. However, the content of biochar made at 300°C possessed the content even higher than the raw material CSM itself, indicating the concentrated organic matter and N-compounds in Char300. Higher pyrolysis temperature coverts biomass to more volatile hydrocarbons with or without N, and non-condensable gases, leading to the decrease in mass yield and low recoveries of OC and N (He et al., 2016a). Phosphorus is mainly present in CSM as phosphate ester compounds (He et al., 2015a; 2017). Their decomposed products are inorganic phosphates that are non-volatile so that the recovery is near 100% and its content is enriched in high temperature biochar with decreased mass. The relatively low P recovery (87.5%) with Char600 might be due to some mass deviation as the low recovery was not observed with the content of P in poultry litter-based Char600 (Guo et al., 2012).

The solid-state ^{13}C NMR spectra of CSM and biochars are shown in Fig. 3. The meal spectrum is typical for organic compound samples (He et al., 2009; Ranatunga et al., 2017). Its peaks can be assigned to functional groups as (1) Alkyl carbons, with the signals near 20 ppm assigned to methyl in hemicellulose and in gossypol, the shoulder at ~15 ppm assigned to methyl end groups in lipid, and the sharp peak near 30 ppm to $(CH_2)_n$ in lipid. (2) Methoxyl (OCH_3) and NCH carbons resonating at ~55 ppm. The signals of OCH_3 are partially selected and retained in the dipolar-dephased spectrum, and its low intensity indicates a smaller contribution of OCH_3 than NCH to the peak near 55 ppm.

(3) O-alkyl carbons including OCH_2 groups (C6 carbons of cellulose) near 64 ppm, OCH groups (C2, C3 and C5 carbons of cellulose or hemicellulose) near 72 ppm, and OCH groups (C4 carbons of cellulose) displaying shoulders at 82 ppm and 88 ppm. (4) Di-O-alkyl carbons with a sharp peak near 105 ppm. (5) C=C carbons (in lipids) and nonoxygenated aromatic carbons (in gossypol) around 110−140 ppm. (6) Oxygenated aromatic carbons (in gossypol) resonating at 148 ppm and 156 ppm. (7) Carboxyl/amide groups resonating near 173 ppm. These identified signals are indicative of the presence of cellulose or hemicellulose (20, 64, 74, 82, 88, and 105 ppm), peptide/protein (55 and 173 ppm), gossypol (20, 116, 130, 137 148, and 156 ppm) and lipid (15, 30, and 129 ppm) in the cottonseed meal.

Table 1. Contents and recovery of organic C, N and P in biochar product

Pyro. T °C	Yield %	%OC		%N		%P	
		Content	Recovery	Content	Recovery	Content	Recovery
CSM*	100	46.54	100	7.23	100	1.27	100
Char300	53.33	55.60	63.71	8.98	66.22	2.27	99.58
Char350	46.68	36.76	36.88	7.17	46.26	2.40	99.83
Char400	40.77	30.24	26.49	5.87	33.10	2.63	100.39
Char450	36.03	25.52	19.76	5.33	26.54	2.66	96.21
Char500	34.97	25.57	19.22	5.01	24.21	2.79	96.13
Char550	33.38	25.83	18.52	4.67	21.56	2.98	97.86
Char600	32.16	25.35	17.52	4.21	18.71	3.05	87.50

* Ash content 7.25%

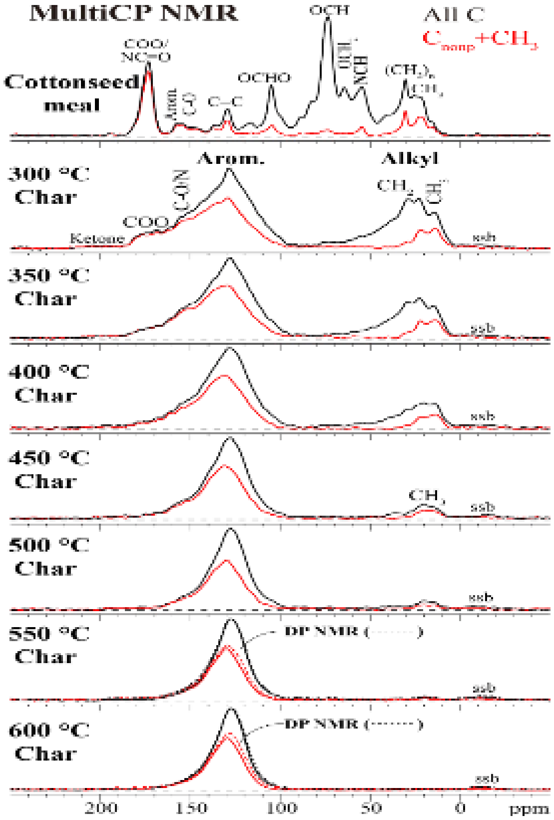

Fig. 3. Multiple cross-polarization (multiCP) 13C NMR spectra

The ^{13}C NMR spectra of biochars produced from defatted cottonseed meal are composed of two major broad bands, assigned to aromatic and alkyl carbons, respectively. For biochar products pyrolyzed at low temperature (< 400 °C), the aromatic carbon peak extends to ~190 ppm due to the overlapping of signals from nonpolar aromatics, O/N-substituted aromatics and carboxyl/ester (COO). The alkyl carbon band contains signals primarily from CH_3, and

CH_2/CH. These observations indicate that pyrolysis even at the lowest temperature (300°C) has transformed biopolymers present in cottonseed meal to aromatic-rich structures. With increasing temperature, the aromatic band becomes much narrower, resulting from the decreased intensity of O/N-substituted aromatics and carboxyl/ester (COO). The alkyl C band, dominated by signals of CH_3 above 400°C, decreases in intensity with temperature and becomes negligible at 550 and 600°C. The near-quantitative results in Table 2 further confirmed the observations.

Table 2. Near-quantitative ^{13}C NMR spectral analysis (% of total ^{13}C signal) of cottonseed meal and its pyrolysis biochars from multiCP spectra and multiCP spectra after dipolar dephasing

Biochar (°C)	Carbonyls		Aromatics			Aliphatic C-O/N		Alkyl	
	C=O	COO	C-O/N	C-C	C-H	O-C-O	C-O/N	C_q/CH/CH_2	CH_3
CSM	0	14	3.5	3	4	9	46	14	6.5
Char300	1	5.5	39		21	5.5		17.5	10.5
Char350	1	4	46		20	4		15	10
Char400	1.5	3.5	49		25	3		9	9
Char450	1	3	56		28	2		3.5	6.5
Char500	0.5	1.5	54		34	2.5		3	4.5
Char550	0.5	1	60		32.5	2.5		1.5	2
Char550[a]	0.5	2	63		28.5	2.5		1.5	2
Char600	1	2	62.5		32	1		0.5	1
Char600[b]	1	2	66		27	2		1	1

[a, b] Functional group composition derived from quantitative ^{13}C direct polarization magic angle spinning spectra.

Per the FT-ICR-MS data, van Krevelen diagrams were created and colored according to the four heteroatom formula groupings (He et al., 2018) (Fig. 4). The van Krevelen diagram is a graphical plot of the elemental H/C versus O/C ratios of molecular formulas and can be used to categorize the components into chemical classes in van Krevelen space. The van Krevelen diagrams showed the presence of lipid-, peptide-, and lignin-like components in both aqueous and oily fractions. While the diagrams of both positive and negative ion mode data show similar patterns in the number of formulas assigned and distribution of compound categories between the two bio-oil phases, the diagrams of the positive ion mode data enhanced the presence of N-containing formulas (as these ionize more readily in positive ion mode). The diagrams showed visually that both fractions possessed low average O/C values, with the CSM-BO-a layer having all formulas at O/C<0.4 (for both positive and negative ion data). The vast majority of formulas for the CSM-BO-o layer were also at O/C<0.4 (especially in positive ion mode), but there were some series that extended out up to O/C 0.8 in negative ion mode. Specifically for CSM-BO-o, most of the formulas fell into the unsaturated hydrocarbon-like region (O/C 0.0-0.1 and H/C 0.7-1.7), but the lipid-like region (O/C 0.0-0.2 and H/C 1.7-2.2) accounted for most of the spectral magnitude, with a significant number of formulas aligning in the lignin-like (O/C 0.1-0.6 and H/C 0.5-1.7) and peptide-like (O/C 0.2-0.6, H/C 1.5-2.2, N/C>0.05) regions. However, the van Krevelen diagrams of positive ion mode FT-ICR-MS show that most of the N species fell in the category of unsaturated hydrocarbons, with some in the lipid-like region. These species should be mainly pyridines and imidazoles (Cole et al., 2013). The van Krevelen diagrams of negative ion mode FT-ICR-MS data show a more diverse distribution of N species, as revealed in the oily and aqueous phases of peanut hull bio-oil (Jarvis et al., 2012). Some specific N species could be isobutyl nitrite, ethyl isocyanide, and 4-methyl-pentanenitrileas reported in switchgrass bio-oil (Cole et al., 2013). As protein was rich in CSM, some peptide-like, and amide compounds, such as aliphatic amides might be also present (Leonardis et al., 2013).

Summary

Defatted cottonseed meal was primarily composed of cellulose/hemicellulose, protein, lipid and gossypol. Pyrolysis of cottonseed meal at 300°C removed signatures of these biopolymers, and produced highly aromatic structures. With increasing temperature, alkyl structures (mainly CH_3 for chars prepared at above 400°C) decreased progressively in intensity and became negligible at high temperatures (550 and 600°C). Meanwhile, O/N-substituted aromatics and carboxyl/ester decreased in intensity, leading to more uniform aromatic ring structures in high-temperature biochar products. Both aqueous and oily fractions of boil-oil produced at 350°C contained lipid-, peptide-, and lignin-like components. However, carbohydrate-like components were found only in the oily fraction. Furthermore, the diagrams revealed more N species in the oily fraction that mostly clustered with O/C<0.2 in the unsaturated hydrocarbon-like region. On the other hand, there were less N species in the aqueous fraction, and they were present mostly in the lipid-like region. This information is useful for both chemical fingerprinting of cottonseed meal/cake-based biochars and bio-oils and guiding the effective uses of these products for soil amendments, environmental remediation, bioenergy resource and industrial feedstock.

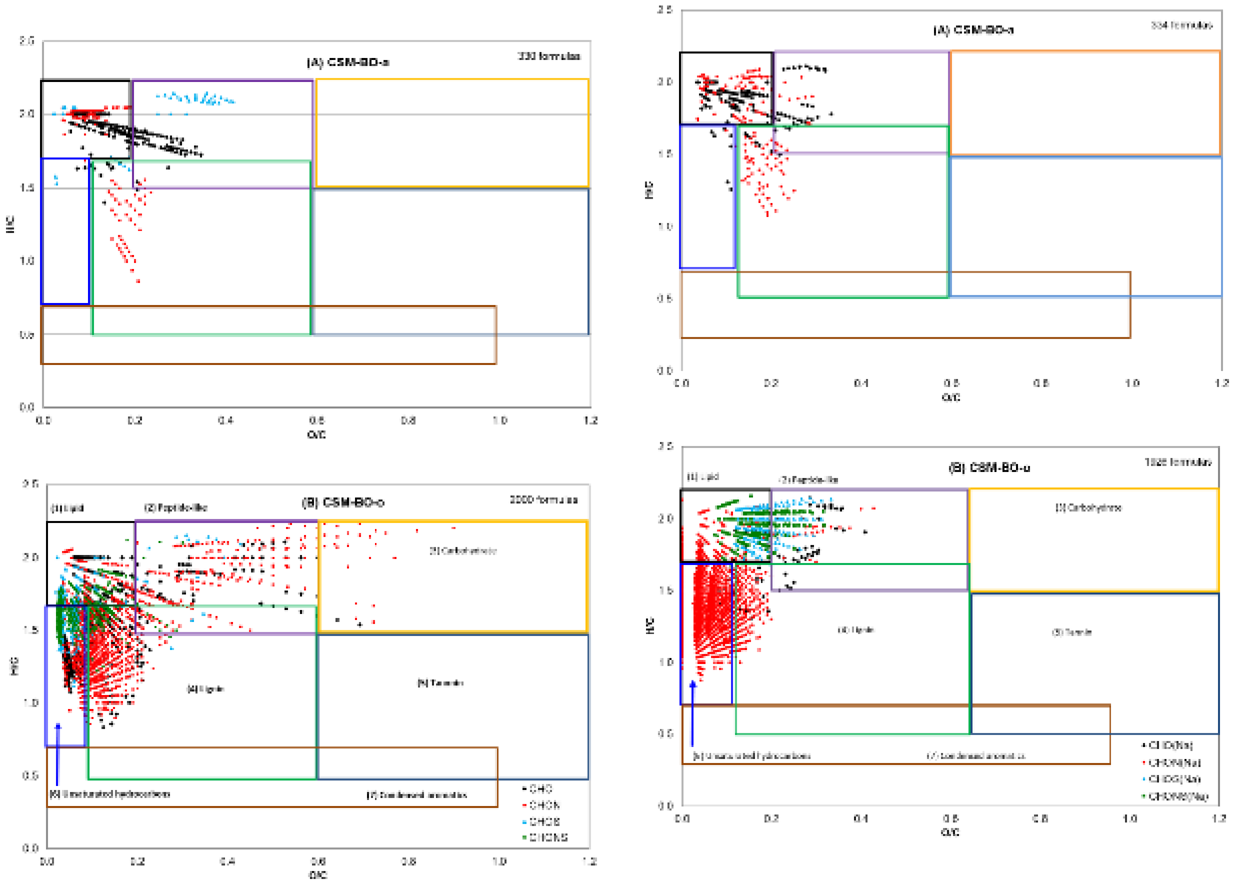

Fig. 4. 2D van Krevelen diagrams from the negative (left) and positive (right) mode ESI FT-ICR mass spectral analysis. Adapted from He et al. (2018).

Acknowledgements

We thank Drs. Xiaoyan Cao (Brandeis University) and Rachel Sleighter (Old Dominion University) for spectroscopic analysis. Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture. USDA is an equal opportunity provider and employer.

References

Cole, D.P., E.A. Smith, D. Dalluge, D.M. Wilson, E.A. Heaton, R.C. Brown, and Y.J. Lee. 2013. Molecular characterization of nitrogen-containing species in switchgrass bio-oils at various harvest times. Fuel 111:718-726.

Guo, M., Y. Shen, and Z. He. 2012. Poultry litter-based biochar: preparation, characterization, and utilization., p. 171-202, *In* Z. He, ed. Applied Research of Animal Manure: Challenges and Opportunities beyond the Adverse Environmental Concerns. Nova Science Publishers, Inc., New York.

He, Z., H. Zhang, and D.C. Olk. 2015a. Chemical composition of defatted cottonseed and soy meal products. PLoS One 10(6):e0129933. DOI:10.1371/journal.pone.0129933.

He, Z., S.M. Uchimiya, and M. Guo. 2016a. Production and characterization of biochar from agricultural by-products: Overview and use of cotton biomass residues, p. 63-86, *In* M. Guo, et al., eds. Agricultural and Environmental Applications of Biochar: Advances and Barriers. Soil Science Society of America, Inc., Madison, WI.

He, Z., H. Zhang, H. Tewolde, and M. Shankle. 2017. Chemical characterization of cotton plant parts for multiple uses. Agric. Environ. Lett. 2:110044 (5 pages). doi:10.2134/ael2016.11.0044.

He, Z., J. Mao, C.W. Honeycutt, T. Ohno, J.F. Hunt, and B.J. Cade-Menun. 2009. Characterization of plant-derived water extractable organic matter by multiple spectroscopic techniques. Biol. Fertil. Soils. 45:609-616.

He, Z., M. Zhang, X. Cao, Y. Li, J. Mao, and H.M. Waldrip. 2015b. Potential traceable markers of organic matter in organic and conventional dairy manure using ultraviolet-visible and solid-state ^{13}C nuclear magnetic resonance spectroscopy. Org. Agr. 5:113-122.

He, Z., M. Guo, R.L. Sleighter, H. Zhang, C.A. Fortier, and P.G. Hatcher. 2018. Characterization of defatted cottonseed meal-derived pyrolysis bio-oil by ultrahigh resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. J. Anal. Appl. Pyro. in press .https://doi.org/10.1016/j.jaap.2018.10.018.

He, Z., K.T. Klasson, D. Wang, N. Li, H. Zhang, D. Zhang, and T.C. Wedegaertner. 2016b. Pilot-scale production of washed cottonseed meal and co-products. Modern Appl. Sci. 10 (2):25-33.

Jarvis, J.M., A.M. McKenna, R.N. Hilten, K. Das, R.P. Rodgers, and A.G. Marshall. 2012. Characterization of pine pellet and peanut hull pyrolysis bio-oils by negative-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. Energy Fuels 26:3810-3815.

Leonardis, I., S. Chiaberge, T. Fiorani, S. Spera, E. Battistel, A. Bosetti, P. Cesti, S. Reale, and F. De Angelis. 2013. Characterization of bio oil from hydrothermal liquefaction of organic waste by NMR spectroscopy and FTICR mass spectrometry. ChemSusChem 6:160-167.

Ozbay, G., and N. Ayrilmis. 2015. Bonding performance of wood bonded with adhesive mixtures composed of phenol-formaldehyde and bio-oil. Ind. Crop. Prod. 66:68-72.

Ozbay, N., A.E. Putun, and E. Putun. 2006. Bio-oil production from rapid pyrolysis of cottonseed cake: product yields and compositions. Int. J. Energy Res. 30:501-510.

Putun, E. 2010. Catalytic pyrolysis of biomass: effect of pyrolysis temperature, sweeping gas flow rate and MgO catalyst. Energy 35:2761-2766.

Putun, E., B.B. Uzun, and A.E. Putnn. 2006. Production of bio-fuels from cottonseed cake by catalytic pyrolysis under steam atmosphere. Biomass Bioenergy 30:592-598.

Ranatunga, T.D., Z. He, K.N. Bhat, and J. Zhong. 2017. Solid-state ^{13}C nuclear magnetic resonance spectroscopic characterization of soil organic matter fractions in a forest ecosystem subjected to prescribed burning and thinning. Pedosphere 27:901-911.

Singh, V., A. Soni, S. Kumar, and R. Singh. 2014. Characterization of liquid product obtained by pyrolysis of cottonseed de-oiled cake. J. Biobased Mat. Bioenergy 8:338-343.

Windeatt, J.H., A.B. Ross, P.T. Williams, P.M. Forster, M.A. Nahil, and S. Singh. 2014. Characteristics of biochars from crop residues: Potential for carbon sequestration and soil amendment. J. Environ. Manag. 146:189-197.

Zhang, Z., D.J. Macquarrie, V.L. Budarin, A.J. Hunt, M.J. Gronnow, J. Fan, P.S. Shuttleworth, J.H. Clark, and A.S. Matharu. 2015. Low-temperature microwave-assisted pyrolysis of waste office paper and the application of bio-oil as an Al adhesive. Green Chem. 17:260-270.