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INVESTIGATOR: KLASSON K T; UCHIMIYA S M; LIMA I M

PERFORMING INSTITUTION:

Agricultural Research Service, Southern Regional Research Ctr
1100 Robert E. Lee Blvd.
New Orleans, LOUISIANA 70124-4305

THERMOCHEMICAL PROCESSING OF AGRICULTURAL WASTES TO VALUE-ADDED PRODUCTS AND BIOENERGY

OBJECTIVES: The research objectives are to develop slow pyrolysis (or torrefaction) and activation processes to convert agricultural feedstock (crop residues, manures, processing wastes, and biorefinery by-products) into: (1) chars that can be used as industrial adsorbents; (2) chars that can be used as soil amendments which improve soil quality, water quality, and sequester carbon; (3) chars that can be used as energy sources (in combustion or gasification); and (4) bio-gas and bio-oil co-products that provide some of the heat and power requirements of the pyrolysis/torrefaction/activation operations and possibly excess heat/power for sale.

APPROACH: The approach will be to take agricultural feedstocks (crop residues, animal manure, and biorefinery waste) and heat them under different gas atmospheres to a set temperature. In order to create chars for target applications, the temperature, heating time, and gas atmosphere will be varied, as well as performing pretreatment (before heating) or post treatment of the chars to obtain desired properties. The products will be tested for target applications in our laboratories and also with collaborators with expertise in ammonia adsorption, soil amendments, bio-oil production, and large-scale pyrolysis.

PROGRESS: 2009/10 TO 2014/10

Progress Report Objectives (from AD-416): The research objectives are to develop slow pyrolysis (or torrefaction) and activation processes to convert agricultural feedstock (crop residues, manures, processing wastes, and biorefinery by-products) into: (1) chars that can be used as industrial adsorbents; (2) chars that can be used as soil amendments which improve soil quality, water quality, and sequester carbon; (3) chars that can be used as energy sources (in combustion or gasification); and (4) bio-gas and bio-oil co-products that provide some of the heat and power requirements of the pyrolysis/torrefaction/activation operations and possibly excess heat/power for sale. Approach (from AD-416): The approach will be to take agricultural feedstocks (crop residues, animal manure, and biorefinery waste) and heat them under different gas atmospheres to a set temperature. In order to create chars for target applications, the temperature, heating time, and gas atmosphere will be varied, as well as performing pretreatment (before heating) or post treatment of the chars to obtain desired properties. The products will be tested for target applications in our laboratories and also with collaborators with expertise in ammonia adsorption, soil amendments, bio-oil production, and large-scale pyrolysis. This is the final report for the project 6435-41000-089-00D that terminated in September 2013. Objectives were transferred to project 6435- 41000-103-00D and will continue until a new project plan can be developed. The project began in October 2009 and significant progress has been made in the last four years, addressing goals of National Program 213 and 306 action plans.

Under Objective 1, we made significant progress in designing biochars for adsorption applications. Unactivated and steam-activated biochars (charcoal created by pyrolysis of biomass) from poultry (chicken or turkey) manure were shown to remove elemental mercury from air and flue- gas streams. It was shown that post-treatment washing sometimes resulted in an improvement in performance but sometimes it was not advantageous to wash the activated chars. We also created activated biochar from almond shells. In a pilot-scale study, this material was used to remove a chlorinated organic contaminant from well water in San Joaquin Valley, CA. We compared collaborators biochars created in a fast pyrolysis with our slow pyrolysis. Fast pyrolysis did not result in any significant development of surface area. Slow pyrolysis, on the other hand, produced a noticeable surface area. Activation of the slow pyrolysis biochars resulted in an increase in the surface area. Activated biochars performed better than slow-pyrolysis biochars which in turn performed better than fast-pyrolysis biochars when we studied removal of metals from water. This pattern was also true when the adsorption of phenol was studied. Activated biochars also helps fermentation of bioethanol. We showed that fermentation inhibitors created by weak acid pretreatment of plant materials could be removed with activated biochar made from flax shive. Under Objective 2, we made significant progress stabilizing contaminants found in soil and groundwater. Both un-activated and steam-activated biochars from chicken litter significantly helped the soil stabilize toxic metals. The poultry based chars were found to serve as an excellent source for phosphorous. Work with collaborators investigated the metal uptake abilities of biochars made from dairy cows, swine, chicken, and turkey manure. In all biochar amendment cases, metal concentrations were lower than in control experiments. In another study, we investigated how the soil type impacted the sorption of several pesticides to the soil. Biochars with greater surface area were better sorbents of the pesticides. In collaboration with Army Research Laboratory and U.S. Department of Defense partners, we demonstrated specific bindings of lead, copper, and zinc by carboxyl surface functional groups of biochar. Under Objective 3, we made progress on investigating the fuel value of biochar. A literature review was conducted to determine the up-to-date knowledge of biochar made from sugarcane bagasse for the use of fuel or co-products. The heating value was calculated for many biochars created by slow pyrolysis at different temperatures, from different raw materials, and for different pyrolysis times. Accomplishments 01 Activated biochars helps fermentation of bioethanol. Fermentation inhibitors created by weak acid pretreatment of plant materials negatively affects bioethanol fermentation. ARS scientists at the Southern Regional Research Laboratory in New Orleans, LA, and at the National Center for Agricultural Utilization Research in Peoria, IL, showed that activated biochars made from agricultural plant waste could be used to either remove fermentation inhibitors or reduce them to the levels that allowed rapid fermentation. It was also shown that the biochars could be left in during fermentation without negative effects. The benefit from this approach is reduced neutralization and separations cost in biofuel-from-biomass approaches that involves acid pretreatment.

PUBLICATIONS (not previously reported): 2009/10 TO 2014/10

1. He, Z., Wang, J.J. 2012. Characterization of plant nutrients and traceable marker components in dairy manure for organic dairy farming management evaluation. In: He, Z., editor. *Applied Research of Animal Manure: Challenges and Opportunities beyond the Adverse Environmental Concerns*. New York, NY:Nova Science. p. 3-19.
2. Guo, M., Shen, Y., He, Z. 2012. Poultry litter-based biochar: preparation, characterization, and utilization. In: He, Z., editor. *Applied Research of Animal Manure: Challenges and Opportunities beyond the Adverse Environmental Concerns*. New York, NY:Nova Science. p. 169-202.
3. Uchimiya, S.M., He, Z. 2012. Calorific values and combustion chemistry of animal manure. In: He, Z., editor. *Applied Research of Animal Manure: Challenges and Opportunities beyond the Adverse Environmental Concerns*. New York, NY:Nova Science. p. 45-62.
4. Miyagi, A., Uchimiya, M., Kawai-Yamada, M., Uchimiya, H. 2013. Impact of aluminum stress on oxalate and other metabolites in *Rumex obtusifolius*. *Weed Research*. 53:(1)30-41.
5. Han, Y., Boateng, A.A., Qi, P.X., Lima, I.M., Jainmin, C. 2013. Heavy metal and phenol adsorption properties of biochars from pyrolyzed switchgrass and woody biomass in correlation with surface properties. *Environmental Management*. 118:196-204.
6. Klasson, K.T., Dien, B.S., Hector, R.E. 2013. Simultaneous detoxification, saccharification, and

ethanol fermentation of weak-acid hydrolyzates. *Industrial Crops and Products*. 49:292-298.

7. Uchimiya, M., Orlov, A., Ramakrishnan, G., Sistani, K. 2013. In situ and ex situ spectroscopic monitoring of biochar's surface functional groups. *Journal of Analytical & Applied Pyrolysis*. 102:53-59.

8. Uchimiya, M., Cantrell, K.B., Hunt, P.G., Novak, J.M., Chang, S. 2012. Retention of heavy metals in a Typic Kandiudult amended with different manure-based biochars. *Journal of Environmental Quality*. 41:1138-1149.
