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Polarity-based separation and chemical characterization of fast pyrolysis bio-oil from poultry litter

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ABSTRACT

140 g Poultry litter pyrolysis oils (PL oils) were separated into four fractions using polarity based fractionation method. Four solvents of increasing polarity (hexane < toluene < chloroform < methanol) were used to sequentially fractionate the PL oil into four fractions (hexane fraction, toluene fraction, chloroform fraction and methanol fraction). The mass of hexane, toluene, chloroform and methanol fractions was 46 g, 29 g, 48 g and 14 g, respectively. The hexane and toluene fractions had low viscosity, while chloroform fraction was viscous and methanol fraction was almost solid at ambient laboratory conditions. The four PL oil fractions were characterized using Fourier Transform Infrared (FT-IR) spectrometry, ^{13}C Nuclear Magnetic Resonance (NMR) spectrometry, and their organic elemental composition and higher heating values were also determined. Furthermore, major compounds in the four fractions were isolated by column chromatography. As a result, four compound classes (fatty acids, sterols, phenols and carbohydrates) and eleven major compounds were isolated from these four fractions. Oleic acid was predominant component of the hexane fraction (48.6%). The major component in methanol fraction was 1, 6-anhydro-β-D-glucose (16.7%), but the chloroform fraction had no predominant component. The 1, 6-anhydro-β-D-glucose and other sugar derivatives were water soluble and were selectively removed from the PL oil by water extraction and this subsequently decreased the viscosity of residual PL oil.

1. Introduction

The USA is the world's largest producer and exporter of poultry meat and the second largest egg producer. About 35 Tg of litter dry matter is generated per year by USA poultry industry and could potentially contribute to soil, water and air contamination by releasing ammonia, greenhouse gases, excess nutrients, pathogens, orders and other substances, which could increase health risks to humans, wildlife and the environment if inappropriately treated [1,2]. The poultry litter is traditionally used as organic fertilizer in agriculture;

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however, due to excess nutrient in the soil, contamination of drinking water and other biosecurity concerns, disposal of poultry litter on agricultural land has become less acceptable [3,4]. At present, the safe and economical disposal of poultry litter is becoming a major problem for the USA poultry industry. Hence, new sustainable strategies and novel technologies are required to deal with the farm wastes. Compared to traditional methods, pyrolysis technology is thought to have great promise to solve this problem. Pyrolysis technology would not only solve the waste disposal and water pollution problems, but also would convert the waste to valuable products such as poultry litter pyrolysis oils (PL oils) and biochar [1,5]. Relative to petroleum products, bio-oils have low higher heating value but lower nitrogen and sulfur contents [6]. Once the world production of conventional fossil fuels begins to fall, it is expected that bio-oils will eventually contribute to the replacement of fossil fuel oil. However, bio-oils have unfavorable physical and chemical properties such as high viscosity, water, oxygen contents and high pH that influence their stability and corrosiveness, thus impacting the fuel quality for heating and transportation. The presence of reactive oxygenates and char particles in the bio-oil affect its stability when stored over time [7,8]. As a result, the bio-oil cannot be used as substitute for fossil fuels unless it can be upgraded or refined.

The chemical composition of biomass pyrolysis oils depends on the composition of the initial feedstock, the production process and the analysis methods. The investigation of the chemical composition of bio-oil produced by the fast pyrolysis of poultry litter revealed the presence of more than 500 compounds, including twelve classes: (a) low molecular weight compounds ($<m/z$ 62), (b) carbohydrates, (c) phenols and lignin monomers, (d) lignin dimers, (e) n-alkylbenzenes, (f) N-heterocyclics, (g) n-fatty acids, (h) n-alkanes, (i) alkenes, (j) sterols, (k) n-diols, and (l) high molecular weight compounds ($>m/z$ 562) [9]. Because of the chemical complexity, the identification of the major compounds of bio-oils remains a challenge. In previous papers, FT-IR (Fourier Transform Infrared), ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectrometry were used to analyze the major components of bio-oil samples. In addition, Curie-point pyrolysis-gas chromatography/mass spectrometry (Cp Py-GC/MS), Pyrolysis field ionization mass spectrometry (Py-FI/MS) and Pyrolysis field desorption mass spectrometry (Py-FD/MS) were applied to identify the compounds of bio-oils [10,11]. However, we still do not have exhaustive understanding of the chemical composition of poultry litter fast pyrolysis oils because of two major problems: The first problem is chemical identification system for different compounds obtained by the application of a particular mass spectrometric method. One approach to overcoming these difficulties is to use different mass spectrometric methods, such as molecular beam mass spectrometry (MBMS), matrix- assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-TOF) and find out how the results compare; the second problem is current GC/MS system can only detect volatile components. However, most compounds accounting for high viscosity of pyrolysis bio-oils, such as oligomeric lignin and carbohydrate compounds, are not easily volatilized during the GC/MS analysis, thus they would not be identified.

The objective of this research is to extract the PL oils by polarity-based separation and isolate and identify the major components in the fractions by using column chromatography (c. c.) for the first time. Compared to published literature [7], this paper emphasizes identification of compound classes that contribute to the aging and high viscosity of poultry litter fast pyrolysis oils (PL oils).

2. Materials and methods

2.1. *Production of bio-oil from poultry litter*

The PL oils were obtained from three-tonne per day transportable mobile fluidized bed pyrolysis unit located at the Heatwole poultry farm at 640 Wheelbarger Road, Dayton, VA. The fluidizing medium was silica sand and fluidizing gas was combustion gases from a mixture of natural gas (10%) and pyrolysis gases (90%). The pyrolysis gases was composed of mostly carbon monoxide (60%), carbon dioxide (30%) and the rest were a mixture of hydrogen and C1–C4 hydrocarbons. The poultry litter had 20% mass fraction moisture and was premixed with Amosoak (10% mass fraction), a proprietary material derived from corn stover to reduce the odor of the poultry litter. The Amosoak was prepared by steam explosion of corn stover at the Virginia Tech Biodesign Bioprocess Research Center (Blacksburg VA). The pyrolysis bed was heated to 450 °C and the poultry liter was fed at 49.89 kg per hour into the fluidizing bed using a rotary gate and screw feeder that fed the litter directly into the hot bed. The pyrolysis products and bio-char were passed through a hot gas filter where the bio-char was separated from the pyrolysis vapors and non-condensable gases. The products were then passed through two condensers in series and two electrostatic precipitators. The first condenser was water-cooled to 50 °C, while the second condenser was cooled with ethylene glycol to 10 °C. The two electrostatic precipitators (Hazen Research Inc, Golden, CO) were set at 20 kV to capture the PL oils. The gases were further cleaned by passing them through a cyclone and a coalescing filter before compressing the non-condensable gases (NCG) to 413.68 kPa for recycling. The NCG stream was split into two fractions, one fraction was used to fluidize the bed and the rest was mixed with a small fraction of natural gas (10%) and air and combusted in a special burner. The hot combustion gases that were devoid of oxygen were passed through the silica sand bed for both fluidization and pyrolysis of the poultry litter. Excess gas was flared into the atmosphere. The PL oils were collected in gallons for various applications. The condenser oils contained large fractions of aqueous fraction whereas the electrostatic precipitator (ESP) fraction and cyclone fractions had very little moisture contents (5% mass fraction). The low moisture content of the ESP oil was attributed to the condensation of most of the water in the two condensers preceding the ESP. Analysis of the organic fraction of the condenser oils showed that they have similar chemical composition as the ESP oil. Thus the ESP oils used in the fractionation experiments are representative of the total oils produced from this plant. The fractionations described below used only the electrostatic precipitator and cyclone oils.