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Research Articles

Characterization of Solid Residues Obtained from Supercritical Ethanol Liquefaction of Swine Manure

[1]Rui Li, [2]Bo Zhang, [2]Shuangning Xiu, [2]Hui Wang, [2]Lijun Wang and [2]Abolghasem Shahbazi

[1]Joint School of Nanoscience and Nanoengineering, North Carolina A and T State University, Greensboro, NC, USA
[2]Department of Natural Resources and Environmental Design, Biological Engineering Program, North Carolina A and T State University, Greensboro, NC 27411, USA

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Corresponding Author:
Abolghasem Shahbazi
Department of Natural Resources and Environmental Design, North Carolina A and T State University, Greensboro, NC, USA
Email: ash@ncat.edu

Abstract: Animal wastes are considered as renewable energy resources, which contain a great energy potential. For this study, swine manure was treated with supercritical ethanol within the reaction temperature range of 240-360°C to produce bio-oil, resulting in a significant amount of solid residues. Solid residues were characterized by using Fourier Transform Infrared (FT-IR), Scanning Electron Microscopic (SEM), surface area, elemental and thermogravimetric (TG) analyses. Solid residues were mainly composed of carbon (26-29 wt%) and ash (35-45 wt%) and exhibited low surface areas (11-17 m^2/g). The analyses indicated an incomplete conversion of lignocellulosic components and thermal chemical reactions including hydrolysis, dehydration, decarboxylation, aromatization and condensation. Supercritical ethanol liquefaction is considered as a feasible way to remove oxygen and utilize carbon and hydrogen in swine manure to produce carbonaceous materials and energy condensed bio-fuels.

Keywords: Swine Manure, Supercritical Ethanol Liquefaction, Solid Residues, FT-IR Analysis, SEM Analysis

Introduction

The increase in pork production resulted in management issues of swine waste (McNab *et al*., 2007). For example, current manure management may cause environmental and public health problems, such as ammonia emission, odor and surface water pollution (Aillery *et al*., 2005). On the other hand, animal wastes are considered to be potential resources of renewable energy. An estimated 5.3 million tons of swine manure is produced annually in the U.S., which could produce biofuels to replace about 6.0 million barrels of petroleum (Cheng *et al*., 2014).

Abundant biomass resources such as agricultural residues, woody residues and animal wastes can be converted into crude bio-oils via two thermochemical processes: pyrolysis or liquefaction (DemirbaŞ *et al*., 2005; Demirbas, 2006). During the pyrolysis process, biomass is heated at temperatures in the range of 450-600ºC in the absence of air to form bio-oil, non-condensable gases and biochar (Wan *et al*., 2009). Liquefaction is used to decompose biomass to produce crude bio-oils in a solvent (water, alcohol, alkanes, phenols, tetralin, or their mixtures, etc.) at a temperature of 250-550°C, under pressure of 5-25 MPa and for reaction time of 5-60 min with/without catalysts (Goudriaan and Peferoen, 1990). Crude bio-oil produced with suitable solvents has a high yield and lower water content. Therefore, liquefaction technology is widely used for high moisture content resources such as animal wastes (Chen *et al*., 2014; Xiu *et al*., 2011), algae (Biller and Ross 2011), sludge (Li *et al*., 2010) and perennial grasses (Zhang *et al*., 2012).

Supercritical fluids are very promising reaction media for chemical conversion of lignocellulosic materials. Because supercritical fluids have gas-like diffusivities and liquid-like density properties, they can enhance the solid solubility in the gas or liquid solvents, promoting the liquefaction reactions. The critical temperature and critical pressure of alcohols such as methanol (239°C, 8.09 MPa) and ethanol (243°C, 6.38 MPa) offered milder reaction conditions than that of water (374°C, 22.1 MPa). In addition, liquefaction with alcohols produced a relatively higher yield of oil products than with water, because alcohols were expected to dissolve relatively higher molecular-weight products derived from biomass due to their lower dielectric constants.

In our previous studies, a supercritical ethanol liquefaction process was applied to convert swine manure into the crude bio-oil (Xiu *et al*., 2010). However, the characteristics of solid residues produced by this process were not evaluated. In the present study, the properties of solid residues were characterized using Fourier Transform Infrared (FT-IR), Scanning Electron Microscopic (SEM), Thermogravimetric (TG) and elemental analyses to understand the mechanism of the supercritical ethanol liquefaction process.

Materials and Methods

Solid Residue Preparation

Swine manure was collected from the farm of North Carolina A&T State University. The air-dried swine manure contained 15.12% cellulose, 19.90% hemicelluloses, 0.88% lignin, 4.86% fat, 17.10% protein, 20.00% moisture and 22.30% ash. The experimental set-up and methods were described elsewhere (Xiu *et al*., 2010). Typically, 30 g of swine manure was treated by using 120 g ethanol as a solvent in a 300 ml autoclave in the reaction temperature range of 240-360°C for 15 min. The obtained solid residues were washed with acetone and then air dried.

Moisture, Ash and Elemental Determination of Solid Residues

The moisture content was determined by using ASTM E871-82 (ASTM, 2006). Ash content was determined by using ASTM D1102-84 (ASTM, 2007).

Elemental analyses for carbon, hydrogen, nitrogen and sulfur contents were determined using a Perkin-Elmer 2400 CHN/S analyzer (Waltham, MA). Carbon, hydrogen and ash were calculated on a dry basis and normalized to an ash-free basis. The oxygen content was calculated by difference. Thus, the oxygen content is slightly larger than the true value since it includes other minor elements.

For calculating the Higher Heating Value (HHV) from elemental analyses, following formula was used (Channiwala and Parikh, 2002):

$$\begin{aligned}\mathrm{HHV(MJ/kg)} = {} & 34.91\times\mathrm{C}+117.83\times\mathrm{H}-10.34\times\mathrm{O} \\ & -1.51\times\mathrm{N}+10.05\times\mathrm{S}-2.11\times\mathrm{Ash}\end{aligned} \quad (1)$$

Surface Area Analysis

Physical nitrogen adsorption was measured by using a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer (Norcross, GA). Each sample was degassed at 200°C for 12 h. The surface area was calculated using the Brunauer-Emmett-Teller (BET) equation.

Thermogravimetric Analyses

Thermogravimetric (TG) analyses were performed simultaneously by using a TA Instruments DSC SDT Q600 Thermogravimetric Analyzer and Differential Scanning Calorimeter (New Castle, DE). Approximately 5 mg of solid residue samples was heated to 900°C at a heating rate 10°C /min under a nitrogen flow.

Scanning Electron Microscopic Analysis

The surface topography of solid residues was measured on a Hitachi SU8000 scanning electron microscope (Tokyo, Japan) operating at a 10 kV accelerating potential. The surface of the sample was sputter coated with gold.

Fourier Transform Infrared Spectroscopy Analysis

Fourier Transform Infrared (FT-IR) spectra were collected on a Varian 670 FT-IR spectrometer (Santa Clara, CA) equipped with a single-bounce diamond Attenuated Total Reflectance (ATR) accessory. Spectra were collected from 4000-500 cm^{-1} with 0.98 cm^{-1} resolution.

Results

Product Yields in Supercritical Ethanol Liquefaction of Swine Manure

The supercritical ethanol liquefaction process of swine manure was performed according to the aforementioned method. In summary, the bio-oil yields were 20.6 wt%, 24.1 wt%, 26.7 wt%, 25.3 wt% and 23.9 wt% at the reaction temperature of 240°C, 260°C, 300°C, 340°C and 360°C, respectively. Meanwhile, 48.5 wt%, 43.1 wt%, 40.1 wt%, 38.6 wt% and 39.8 wt% of the feedstock were converted into solid residues, respectively (Xiu *et al*., 2010).

Physical Properties of Solid Residues

Physical Properties

The bulk chemical compositions of solid residues derived from swine manure are shown in Table 1. The carbon content in the solid residues was in the range of 26.7-28.9 wt%, which is lower than that of swine manure. The amount of carbon in solid residues inversely correlated to the bio-oil yield. The solid residue with the lowest carbon content and the highest oxygen content was obtained at 300°C, at which the bio-oil reached the highest yield of 26.7 wt% with the highest carbon content of 73.66 wt% and the lowest oxygen content of 11.48 wt%. Estimated higher heating values from the elemental composition of

solid residues ranged from 3.71 to 5.57 MJ/kg. The highest higher heating value of bio-oil of 33.98 MJ/kg was reached at 300°C, at which the lowest higher heating value of solid residue was 3.71 MJ/kg. The ash content of solid residues is in the range of 35.3-45.6 wt%, which is almost twice as high as that of swine manure (~20.9 wt%) at the expense of carbon. In general, the ash content increased with liquefaction temperature. As shown in Table 1, the BET surface area of swine manure was 1.18m^2/g and the surface area of solid residues ranged between 11-17 m^2/g, which was associated to non-porous solids.

Thermogravimetric Analyses

The TG and DTG curves of solid residues and swine manure exhibited their weight loss characteristics (Fig. 1). The starting and final temperatures of decomposition were defined on the DTG curve, corresponding to the intersection of the tangent line with the curve. The decomposition of swine manure can be divided into three phases (Fig. 1b). The first phase (T<120°C) was moisture removal. Between 165-200°C, the weight loss for devolatilization was 2.86 wt%. The decomposition occurred between 220-540°C with weight loss of 30.4 wt%. The devolatilization peak at 180°C existing in swine manure disappeared from solid residues, indicating that volatile compounds such as fat were decomposed completely during the liquefaction process. The starting temperature of decomposition for solid residues between 220°C and 540°C shifted towards higher temperature as reaction temperature increased.

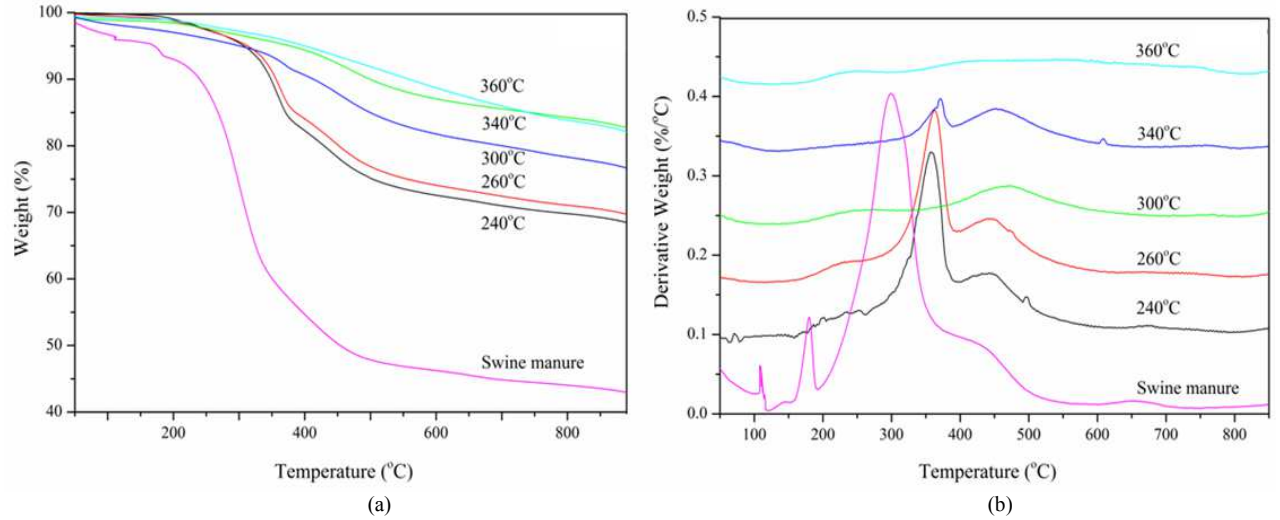
Scanning Electron Microscopy

The morphologies of swine manure and solid residues are shown in Fig. 2. Figure 2a exhibited arranged cellulose network. Even at higher liquefaction temperature of 360°C, the biomass natural macrostructure still persisted (Fig. 2b-f). Partially broken polymers confirmed that the surface of solid residues was nonporous and irregular sub-micro size particles with different shapes and sizes were observed.

Fourier Transform Infrared Spectroscopy

In Fig. 3, the FT-IR spectra show organic functional groups of swine manure and liquefaction derived solid residues. Spectral peaks were interpreted based on previous reports (He *et al*., 2013; Li and Shahbazi, 2015; Schnitzer *et al*., 2007; Zhang *et al*., 2014). The intensity of -OH groups (a broad band between 3600 and 3000 cm^{-1}) of solid residues was much lower than their corresponding swine manure's and the -OH peak intensity of solid residues decreased as liquefaction temperature increased. Intensities of bands (2920 and 2850 cm^{-1}) were associated with aliphatic C-H stretching vibration. The peaks in solid residue became less intensive, suggesting that dehydration reactions were enhanced by increasing temperature.

The bands at 1650, 1543 and 1314 cm^{-1} implied the stretching vibration of C=O of primary amides (amide I), N-H bending vibrations of secondary amides (amide II) and C-N stretch of primary amines, respectively. The weak peaks indicated that the decomposition of protein can occur at 240°C. The peak (1552 cm^{-1}) was attributed to asymmetric stretching of C=O in carboxylic groups.



(a) (b)

Fig. 1. TG (a) and DTG (b) curves of solid residues and swine manure

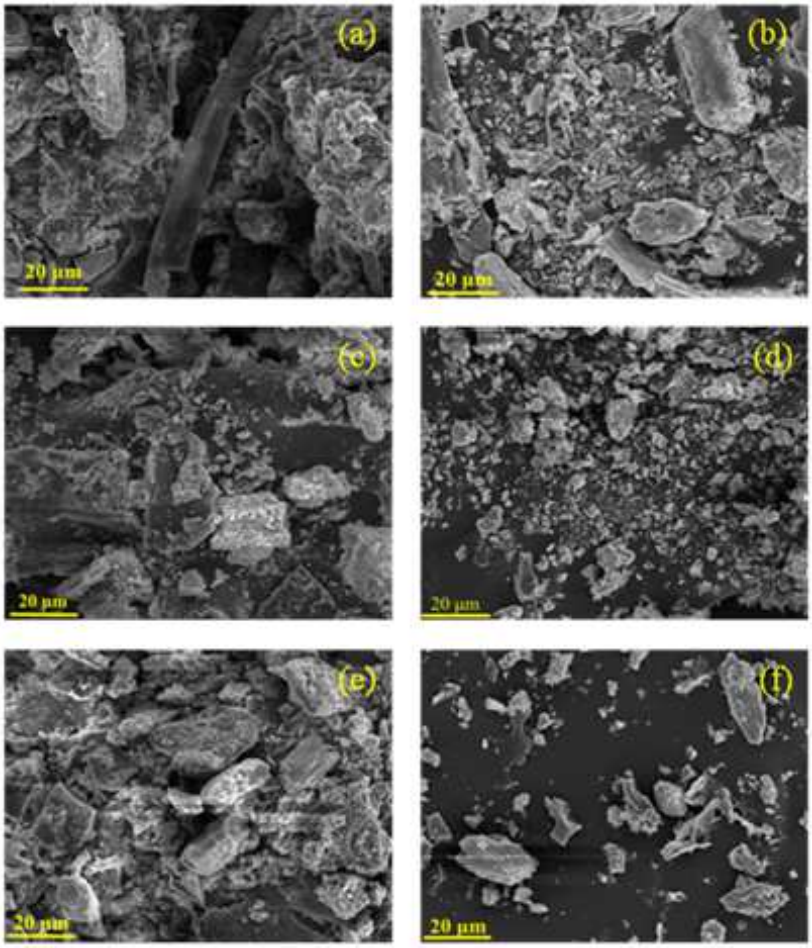


Fig. 2. SEM micrographs of solid residues and swine manure. The solid residues were obtained from supercritical ethanol liquefaction of (a) swine manure, (b) at 240°C, (c) at 260°C, (d) at 300°C, (e) at 340°C and (f) at 360°C

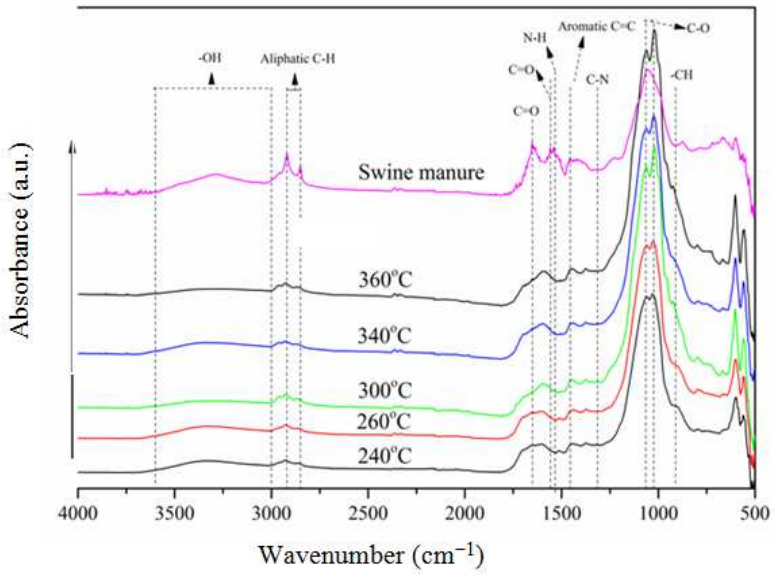


Fig. 3. FT-IR spectra of solid residues and swine manure

Table 1. Composition analysis, heating value and surface area of solid residues

Solid residues obtained at (°C)	Elemental composition (wt%)[a] C	H	N	S	O	Moisture[b] (wt%)a	Ash[b] (wt%)	HHV[c] (MJ/kg)	Surface area[d] (m^2/g)
240	26.83	2.82	2.54	0.61	67.20	3.75	35.29	5.02	17.30
260	28.22	2.85	2.62	0.59	65.72	3.39	41.18	5.57	17.28
300	26.77	1.89	2.38	0.36	68.60	1.95	37.50	3.71	11.56
340	28.16	2.15	2.70	0.47	66.52	3.65	41.67	4.63	12.40
360	28.91	2.01	2.49	0.46	66.13	2.06	45.61	4.68	12.59
Swine Manure	34.86	5.51	3.34	1.04	55.25	4.12	20.87	12.53	1.18

a. Moisture free basis
b. Samples were air-dried.
c. The higher heating values were calculated according to Channiwala's formula.

This missing peak indicated that decarboxylation reaction occurred, which caused the release of carbon in the form of CO_2. The peak (1455 cm^{-1}) corresponded to the C=C stretching vibration in aromatic ring in lignin. The still presented peaks in all samples indicated that lignin fragments remained. The absorbance of the dominant C-O (1064 and 1024 cm^{-1}) stretch associated to the β-glycosidic bond in cellulose and hemicellulose. Only partial cellulose and hemicellulose were liquefied during the treatment. The peak (910 cm^{-1}) was attributed to the out-of-plane bending vibration in aromatic nucleus -CH, which suggested the occurrence of aromatization. These changes in peaks revealed that carbon aromaticity was obtained.

Discussion

A lower carbon content in solid residues resulted in a decreased HHV. These values indicated that the energy content in swine manure was mostly transferred into the bio-oil. The results of elemental analysis were slightly different from our previous study (Xiu *et al*., 2010), because the previous protocol didn't include sulfur measurement and the moisture contents were different too. When combining the results of both studies, the empirical formula of the swine manure, solid residues and bio-oil were determined as $C_{186}H_{350}N_{15}O_{221}S_2$, $C_{154}H_{155}N_{12}O_{278}S$ and $C_{156}H_{245}N_8O_{29}$, respectively.

SEM analysis only showed irregular sub-micro size particles with different shapes and sizes and there were no hydrothermal spherical carbons as synthesized via HTC (Yan *et al*., 2015), because the residence time (15 min) was too short to form.

The FT-IR spectra of all solid residue samples were similar. Almost no new types of functional groups formed after liquefaction and difference in the intensity of some peaks indicated that some reactions such as dehydration, decomposition of protein, decarboxylation and aromatization happened.

Conclusion

A significant amount of solid residues was produced during supercritical ethanol liquefaction of swine manure. The solid residues were composed of amorphous carbonaceous materials (26-29 wt%) and inorganic ash (35-45 wt%), with low surface areas (11-17 m^2/g). FT-IR spectra and SEM indicated incomplete conversion of lignocellulosic components.

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Author's Contributions

Rui Li: Made substantial contributions to conception and design, analysis and interpretation of the data, collection and assembly of data, drafting of the article, critical revision of the article for important intellectual content and final approval of the article.

Bo Zhang: Made substantial contributions to analysis and interpretation of the data, critical revision of the article for important intellectual content and final approval of the article.

Shuangning Xiu: Made substantial contributions to critical revision of the article for important intellectual content and final approval of the article.

Hui Wang: Made substantial contributions to critical revision of the article for important intellectual content and final approval of the article.

Lijun Wang: Made substantial contributions to critical revision of the article for important intellectual content and final approval of the article.

Abolghasem Shahbazi: Made substantial contributions to obtaining of funding, administrative support, critical revision of the article for important intellectual content and final approval of the article.

Ethics

This article is original and contains unpublished material. The corresponding author confirms that all of the other authors have read and approved the manuscript and no ethical issues involved.

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