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Reductive hydrothermal treatment of sewage sludge

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Abstract

The United States and the European Union each generate around 6900 million dry tons of sewage sludge annually. This is disposed of by land application, landfilling, incineration and other approaches. Reductive hydrothermal (HT) treatment refers here to simple aqueous systems heated and pressurized above 300 °C/100 bar under anoxic and/or reducing conditions. The purpose of this study was to examine the HT treatment of municipal sewage sludge and infectious fecal microbial cultures with respect to waste volume reduction, biological sterilization, and the generation of usable hydrocarbon product mixtures. These endpoints from HT treatment also were compared to those from pyrolysis. HT at 400 °C/150 bar transformed sewage sludge solids into complex gas phase (4%) and liquid (6%) hydrocarbon mixtures (approximately 11% combined yield), along with similar amounts (5%) of solid residues. HT products in the aqueous phase (e.g., alcohols) were present but not analysed. Viable mixed fecal cultures (10^9 colony forming units/mL) were completely sterilized by HT treatment, and a hydrocarbon mixture also was generated from the cells, but it was markedly different from that resulting from HT of the sludge. The hydrocarbon assemblage generated from the sludge included *n*-hydrocarbons (C_9–C_{20}) and alkyl substituted benzenes, phenols, and related compound series of higher mass (e.g., indanes, naphthalenes). Light aromatic parent compounds were significantly less abundant than their substituted C_1–C_5 alkyl series and there was a paucity of N–, O– and S–heterocycles and polycyclic systems with more than three fused rings. This was different from the products of pyrolysis which were dominated by a relatively simple mixture of linear and branched hydrocarbons and their oxidized homologues (e.g., aldehydes).

1. Introduction

High volume waste biomass (WB) is generated in wood and agricultural product development (e.g., timber, cuttings, paper, decommissioned utility wood, sugar cane wastes), food and pharmaceuticals R and D and production (e.g., biohazardous materials, spent media, food processing byproducts and wastes) and urban system maintenance (e.g., municipal sludge, vegetation, organic garbage, hydrocarbons). WB possesses residual energy that can be recovered and/or used as substrates in the synthesis of desirable products. So, WB can be viewed as a resource in at least those cases where: (1) energy return on process investment is favorable or competitive with existing sources (e.g., biofuels from crops), and/or (2) when use of the WB lessens environmental or human effects related to continued disposal of a waste in other ways.

Currently the US generates some 6900 million dry tons of sewage sludge annually, with 41% added to agricultural land, 17% placed in landfills, 22% incinerated, and the remainder (20%) handled in “other” ways (US EPA, 1999; National Research Council, 1984; Water Science and Technology Board, 1993). The European Union generates approximately the same amount annually, with application rates to agricultural lands somewhat higher (UK Ministry of Agriculture, Fisheries and Forests Department, 1993). The rate of production in both the EU and US is growing slowly.

The recycling/use of sewage sludge presents a series of challenges because of its heterogeneous nature: pathogens,

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toxic metals and organic chemicals, eutrophicants (e.g., N and P compounds), solids, and inorganic material occur together in widely varying proportions. For example, metal/toxic organic contaminants in some sewage sludge can preclude use direct incineration or use as a fuel, and, along with pathogens, also affect its desirability for use on agricultural soil. These and related issues front an ongoing international debate on the proposed uses/disposal options of municipal sewage sludge (US EPA, 1999; UK Ministry of Agriculture, Fisheries and Forests Department, 1993; National Research Council, 1984; Water Science and Technology Board, 1993).

Reductive hydrothermal (HT) treatment refers here to aqueous systems (e.g., suspensions, solutions, slurries) heated and pressurized above about 300 °C/100 bar under anoxic or more reducing electrochemical conditions in the bulk phase. Unlike supercritical wet oxidation (SWO) and related partial oxidation approaches (Junk et al., 1997), HT conditions intentionally maximize the generation of gas and liquid phase reduced products (e.g., hydrocarbon mixtures) from a broad range of WB. Important transformation reactions occur on time scales of minutes–hours, depending on process reaction conditions including T, P, substrate physical parameters, co-reactants, and other variables (Junk and Catallo, 1996, 1997; Holgate and Tester, 1994; Boock and Klein, 1993; Ikushima, 1994). Previous work has examined the HT transformation of decommissioned utility pole wood treated with creosote (Catallo and Shupe, 2003), copper arsenates and pentachlorophenol (Catallo et al., 2004), pest vegetation (Shupe and Catallo, 2006; Catallo et al., 2007), algae, and agricultural and food industry wastes under simple conditions in situ and minimal pretreatment processing (i.e., no added reactants, no conditioning reactions). Data confirmed that closed-loop and batch treatment of biomass yielded gas and liquid hydrocarbon mixtures, water soluble compounds, and also allowed for recovery or destruction of toxic organic chemicals and recovery of metals (Catallo and Shupe, 2003; Catallo et al., 2004).

The purpose of this study was to explore the hydrothermal treatment (HT) of municipal sewage sludge and mixed fecal cultures with respect to resulting volume reduction (percent of the initial sewage sludge solids eliminated), generation of volatile and semi-volatile chemical mixtures, and biological sterilization. As is appropriate for a first pass, the conditions used in this work were minimal: no co-reactants, catalysts, or other materials were used.

2. Methods

2.1. HT reactors

The reactors used in this work were designed in-house and fabricated at commercial machine shops from corrosion-resistant alloys. These included batch vials with internal volumes 6 mL for rapid heating/cooling, and larger 65 mL systems equipped with gas and liquid sampling accesses. Reactors were charged with water and WB substrate (in this case: sewage sludge or fecal bacterial pellet, below) to give dilute slurries of about 29 mg/mL. The slurries were deoxygenated by Ar (60 min) sparging, and the reactors then were sealed under an Ar blanket. The reactors were added to preheated, feedback-controlled furnaces for total reaction times of up to 4 h at 400 ± 0 °C, including heat up; with pressures reaching 200 bar during treatment. After treatment, the HT (and control reactors) were immersed in a water bath for 20 min. At room temperature, liquid samples were collected from the reactors and extracted repeatedly in DCM (2:1 DCM:sample, v/v) as summarized below. The mass of volatile compounds generated by HT treatment was estimated by passing the gas phase product mixture through a gas-tight (SnoTrik™) stainless steel feed line from the HT reactor to an acetone-dry ice cold trap (−70 °C). The trapped, condensed volatiles then were weighed. Pyrolysis of sewage sludge was performed as described above for HT except that the substrate sewage sludge mass was wetted with water to 50% on a weight basis. Pyrolysis temperature was 400 °C for 4 h (as above), with pressure <10 bar.

2.2. Sewage sludge

The sewage sludge used for all experiments was a dirt brown, fine solid material from a medium capacity 380 m^3/day secondary wastewater treatment plant which handled dedicated municipal sewer feeds with no contribution from farm, industrial or street overflow sources. After skimming and gravitational settling, the sludge was lime precipitated in an anaerobic digester prior to collection and drying. The dried material, mixed to 29 mg/mL with pure water (pH 6.8), gave a pH of 8.5.

Samples (10 g) for HT controls (no HT treatment) were weighed into clean cellulose thimbles and Soxhlet™ extracted using ultra-pure dichloromethane (DCM). The DCM extract was dried using anhydrous Na_2SO_4, concentrated under dry N_2 gas, and then analyzed by gas chromatography–mass spectrometry (GC–MS; below) for semi-volatile organic chemicals (e.g., Fig. 1) including petroleum hydrocarbons (e.g., alkanes/alkenes, cycloalkane/alkenes, aromatic hydrocarbons, and polycyclic aromatic hydrocarbons of less than six rings), N–, O– and S– heterocyles, and selected industrial pollutants (e.g., chlorinated aromatics). As hydrocarbons were an important endpoint in this HT application, analysis of control samples was designed to detect any semi-volatile compounds already present in the sludge. As HT treatment can result in 99% mass reduction in the WB substrate, controls were concentrated by a factor of at least 100×.

2.3. Fecal microbial cultures

Fresh human fecal samples were swabbed into in brain heart infusion (Difco) broth in glass flasks using standard sterile techniques. The inoculated and control (sterile swabs