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Short Communication

Formation and degradation of valuable intermediate products during wet oxidation of municipal sludge

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HIGHLIGHTS

- Fermented municipal sludge was treated by non-catalytic wet oxidation.
- A significant formation of acetic acid occurred within the wet oxidation process.
- High molecular weight intermediates were converted into simpler acids.
- The severity of wet oxidation process affects the formation of intermediates.

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ABSTRACT

The current study investigated the formation of organic acids and alcohols as major intermediate products of wet oxidation of municipal sludge. Municipal sludge was subjected to 60-min wet oxidation at temperatures ranging from 220 to 240 °C, with 20 bar oxygen partial pressure. Acetic acid was the main intermediate compound produced in this study, followed by propionic, n-butyric, iso-butyric and pentanoic acids and methanol. It was found that the process severity has a significant influence on the formation and degradation of these intermediate products.

1. Introduction

Municipal sludge is the semi-solid residue remaining at the end of a municipal wastewater treatment process. It can be generally described as a water-based suspension containing suspended particles, fibrous material and dissolved substances, mainly weakly biodegradable organic compounds and pathogenic organisms such as viruses and bacteria. Municipal sludge is also rich in valuable organic compounds and nutrients. The continued increase in the volume of municipal sludge from wastewater treatment plants, coupled with strong regulatory drivers such as increasing its reuse, recovery and recycling have called for alternative disposal and treatment processes for this material. These factors are increasing the need for alternative disposal and treatment processes that can address the unique challenges of municipal sludge.

Wet oxidation is a hydrothermal treatment technology capable of treating municipal sludge. It is particularly applicable for wastes with high concentrations of organic matter or toxic contaminants (Baroutian et al., 2015). There have been several commercial treatment plants using wet oxidation to process municipal sludge, as well as waste streams from petrochemical, chemical and pharmaceutical industries, including the Athos, VerTech and Zimpro processes (Andrews et al., 2015; Hii et al., 2014).

Wet oxidation involves aqueous phase deconstruction of organic and oxidisable inorganic components at sub-critical temperature and pressure (150–320 °C and 20–150 bar) in the presence of oxygen (Baroutian et al., 2013b). The process has four major potential outcomes: (i) degradation and removal of organic compounds, (ii) reduction of mass and volume (>90%), (iii) destruction of pathogens and sterilisation of material, and (iv) recovery of valuable compounds (Baroutian et al., 2015; Prince-Pike et al., 2015). One of the advantages of wet treatment technologies is that it avoids the need for the energy-intensive dewatering step, and can directly process liquid and slurry municipal sludge.

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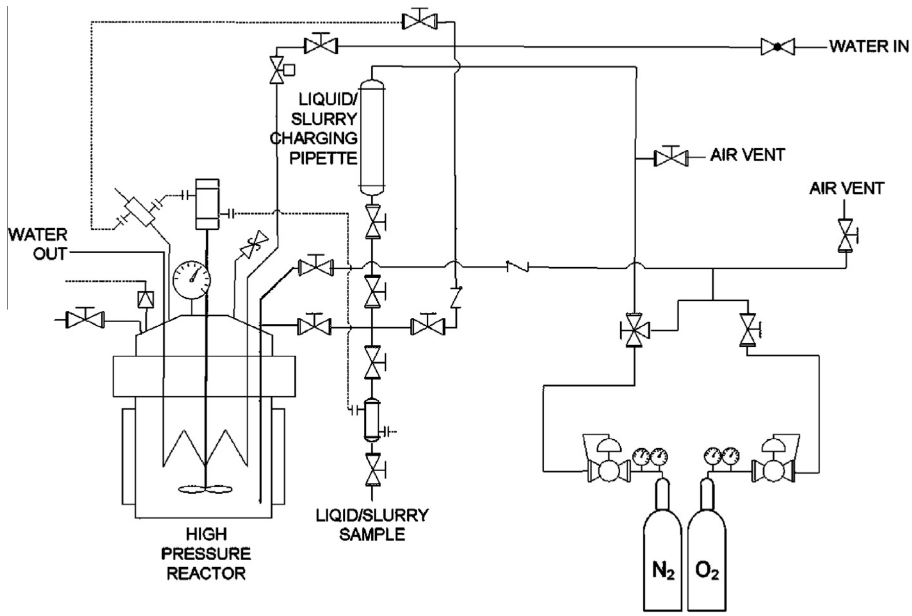

Fig. 1. Schematic diagram showing experimental wet oxidation reaction set-up.

During wet oxidation of sludge a large proportion of the insoluble organics are first solubilised through hydrolytic depolymerisation reactions which, together with the formation of free radicals, are the most important oxidising species. Subsequent oxidative reactions convert these hydrolysis products into increasingly simpler organics such as organic acids and alcohols. Finally, these products can be further oxidised to CO_2, N_2, water and residual ash (Debellefontaine and Foussard, 2000; Li et al., 1991; Robert et al., 2002).

The mechanism of the oxidation process based on free radical chain reactions: (i) initiation – reaction of molecular oxygen with organic compounds (RH) to produce alkyl (R$^{\cdot}$) and hydroperoxyl (ROO$^{\cdot}$) radicals, or production of alkyl (R$^{\cdot}$) and hydrogen (H$^{\cdot}$) radicals through non-oxidative hydrothermal reactions; (ii) propagation – further reactions of oxygen and other organic and inorganic radicals to produce strong oxidant hydrogen peroxide (H_2O_2); and (iii) oxidation – adding organic acid links (OOH) to the organic fragments which results in the formation of organic acids (Robert et al., 2002; Shanableh and Jomaa, 2001).

Organic acids (mainly acetic acid) are the major intermediate products of municipal sludge and biomass. The worldwide production of acetic acid is about 7 million tonnes per year (US$ 600–800 per tonne) (Lee et al., 2007). Production of organic acids, specifically acetic acid, during hydrothermal treatment is highly desirable because these compounds consist of small, readily degradable compounds that form a suitable substrate for beneficial uses – including methanogenic fermentation and biofuel and/or biopolymer production in a subsequent downstream process (Shanableh, 2000; Strong and Gapes, 2012).

Given the potential applications and the increasing need for organic acids for various purposes, investigation of the production and recovery of these acids from organic wastes and renewable resources has received increasing attention in recent times. The wet oxidation process has been around for many years and has gained a renewed burst of interest since 2000. Shanableh (2000) compared production and removal of organic acids, mainly acetic acid, from sludge using wet oxidation at subcritical (<374 °C) and supercritical (>374 °C) conditions. In another study, Shanableh and Jomaa (2001) comparatively investigated the formation and degradation of organic acids produced from primary, secondary and a mixed sludges using wet oxidation. Chung et al. (2009) and Baroutian et al. (2015) studied the influences of operational conditions on sludge degradation and organic acids formation in wet oxidation process. Strong et al. (2011) examined destruction of municipal sludge and production of organic acids using wet oxidation treatment followed by anaerobic fermentation. Andrews et al. (2015) investigated production of acetic acid from municipal sludge using a two-step biological-wet oxidation process at pilot scale.

Most of these studies have dealt with different raw materials or have suggested combined techniques and new approaches for the handling of municipal sludge and for the resource recovery. However, detailed investigations on the formation of intermediate organic acids are still lacking. Moreover, most of these studies have used a slow batch heat-up over time before the desired temperature was reached. This approach could add complexity to experiment lead to changes in the fundamental characteristics of the materials prior to the initiation of the wet oxidation conditions under study (Baroutian et al., 2015). Therefore, it is anticipated that by injecting material in a pulse dosing fashion into a system already at temperature, the reactions of interest can be better studied as they occur under the described thermal conditions.

This study was designed to investigate the formation of organic acids as major intermediate products of the wet oxidation of municipal sludge. This study made an attempt to address the question of how the intermediate organic acids are formed, and how their production is influenced by the process parameters.

2. Methods

2.1. Materials

An anaerobically digested municipal sludge was used for the experiments. The sludge feed material was obtained from the Rotorua Lakes Council (RLC) wastewater treatment plant in Rotorua, New Zealand. The sludge consisted of approximately 40% primary and 60% secondary sludge obtained from the belt presses at the processing plant. Municipal sludge is a good example of organic solid waste: it is typically composed of protein (the dominant constituent), carbohydrates (mainly cellulose) and fatty acids (Baroutian et al., 2013a). Samples of the fermented sludge were frozen at −20 °C until use.