Bioresource Technology 146 (2013) 294–300

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Transformation and removal of wood extractives from pulp mill sludge using wet oxidation and thermal hydrolysis

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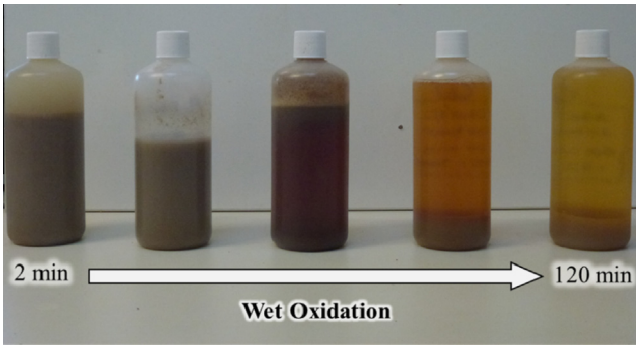
HIGHLIGHTS

- Pulp mill sludge was treated by wet oxidation or thermal hydrolysis.
- Wet oxidation caused rapid and near-complete destruction of wood extractives.
- Thermal hydrolysis was found to be ineffective in degrading extractive compounds.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 31 May 2013
Received in revised form 19 July 2013
Accepted 22 July 2013
Available online 27 July 2013

Keywords:
Wet oxidation
Thermal hydrolysis
Pulp mill sludge
Wood extractives

ABSTRACT

In order to remove wood extractive compounds from pulp mill sludge and thereby enhancing anaerobic digestibility, samples were subjected to either oxidative hydrothermal treatment (wet oxidation) or non-oxidative hydrothermal treatment (thermal hydrolysis). Treatments were carried out at 220 °C with initial pressure of 20 bar. More than 90% destruction of extractive compounds was observed after 20 min of wet oxidation. Wet oxidation eliminated 95.7% of phenolics, 98.6% fatty acids, 99.8% resin acids and 100% of phytosterols in 120 min. Acetic acid concentration increased by approximately 2 g/l after 120 min of wet oxidation. This has potential for rendering sludge more amenable to anaerobic digestion. In contrast thermal hydrolysis was found to be ineffective in degrading extractive compounds. Wet oxidation is considered to be an effective process for removal of recalcitrant and inhibitive compounds through hydrothermal pre-treatment of pulp mill sludge.

1. Introduction

Lignocellulosic sludge is a major solid waste product of the pulp manufacturing industry. Increased costs of landfill waste management, as well as increased public and government pressure to limit the waste to landfill, have compelled industries to consider alternative waste management solutions. Anaerobic digestion of this material is an attractive disposal route as it both reduces the amount of final sludge solids for disposal and enables the process to generate a product in the form of biogas (Park et al., 2012; Saha et al., 2011; Strong et al., 2011a).

Solid waste from softwood pulp mills often contains high levels of wood extractives (Das et al., 2012; Leach and Thakore, 1978; Vepsäläinen et al., 2011; Verta et al., 1996). These extractives are a group of lipophilic chemical compounds that includes triglycerides, fatty acids, resin acids, sterols, phenolics, sterol esters, and monoterpenes released from wood during the pulp processing.

Many of these compounds are not easily degraded under anaerobic digestion conditions. The resin acid fraction is the dominant extractive component of softwoods. This fraction may inhibit

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http://dx.doi.org/10.1016/j.biortech.2013.07.098

Table 1
Anaerobic treatability of pulp mill effluent from different processes (Rintala and Puhakka, 1994).

Waste origin	COD (mg/l)	Anaerobic degradation (%)	Major methanogenesis inhibitors
Wet debarking	1300–4100	44–78	Resin acids
Thermo-mechanical pulping	1000–5600	60–87	Resin acids
Chemo-thermo-mechanical pulping	2500–13,000	40–60	Resin acids, fatty acids
Chlorine bleaching	900–2000	30–50	Resin acids, phenolics

biological growth and methane production if not degraded (Sekido et al., 1990). Sierra-Alvarez (1990) studied the impact of resin acids on anaerobic treatment of forest industry wastewater and found that they were responsible for inhibiting 50% of methanogenesis at concentrations of 20–330 mg/l. Anaerobic treatability of pulp mill effluent from different processes and the major methanogenesis inhibitors found in these wastes are given in Table 1 (Rintala and Puhakka, 1994).

Methods for effective removal of these components are needed so that methanogenic energy production from pulp manufacturing waste can be maximised.

Hydrothermal processing is a potentially useful waste management option. Two positive aspects of this process are simultaneous waste degradation and formation of industrially useful by-products. Hydrothermal processing involves aqueous phase deconstruction of organic and inorganic components at elevated temperatures and pressures. The reactions are completed in the water phase, thus eliminating the need for water removal prior to treatment. This is an advantage over thermal technologies such as incineration, gasification and pyrolysis. Hydrothermal processing of solid waste has four major objectives based on application: (I) enhancement of fermentation, (II) degradation and removal of organic compounds, (III) reduction of mass and volume (Strong and Gapes, 2012) and (IV) recovery of valuable compounds (Strong et al., 2011a; Yoshida et al., 2003).

Hydrothermal processing can involve either non-oxidative or oxidative reactions. Examples of each type are thermal hydrolysis (non-oxidative) and sub-critical wet oxidation (oxidative). Thermal hydrolysis is generally used as a pre-treatment for the anaerobic digestion of sludge, especially in municipal wastewater treatment plants (Keymer et al., 2013; Morgan-Sagastume et al., 2011; Shana et al., 2013). Use of temperatures in the range 100–175 °C at low pressure (max. 13 bar) results in depolymerisation. Depolymerisation facilitates biological degradation, decreases sludge viscosity and increases dewaterability (Abelleira et al., 2012; Haug et al., 1978; Tanaka et al., 1997). Temperatures of 160–180 °C have been found to be an optimal for thermal hydrolysis of sludges in previous studies (Abelleira et al., 2012; Wilson and Novak, 2009).

Above this range thermal hydrolysis results in a sharp reduction in biodegradability (Bougrier et al., 2008; Wilson and Novak, 2009) due the formation of recalcitrant soluble organic compounds (Bougrier et al., 2007).

Wet oxidation involves the liquid phase oxidation of organic or oxidisable inorganic compounds at elevated temperatures and pressures using oxygen (applied as air or pure oxygen). Typical conditions for wet oxidation are 150–320 °C under 20–150 bar of pressure for 15–120 min (Zou et al., 2007).

Several recent studies have indicated a renewed interest in hydrothermal processing due to inherent advantages in the handling of wet waste and the potential for resource recovery from waste (Abelleira et al., 2012; Blöcher et al., 2012; Chen et al., 2012; Strong and Gapes, 2012; Strong et al., 2011a). Verenich et al. (2000) investigated wet oxidation of concentrated wastewaters from paper mills as a method for reducing the concentration of organic material and improving their biodegradability. Strong and Gapes (2012) studied pre-treatment of pulp mill solids by wet oxidation and thermal hydrolysis. Wood et al. (2009) used thermal hydrolysis to increase the extent and rate of anaerobic bioconversion of pulp mill sludge into biogas.

These studies have identified the efficiency of hydrothermal processes for treatment of pulp mill sludges. It was also shown that selective destruction or removal of extractive compounds would reduce the resistance of solid waste to methanogenesis. However there is a lack of information regarding the destruction of extractive compounds during hydrothermal processing. The current study was designed to investigate the wood extractive compounds during wet oxidation and thermal hydrolysis processes. The specific aim was to ascertain the potential for the destruction of extractives through wet oxidation working on the hypothesis that oxidative conditions would provide a destructive influence, rather than thermal hydrolysis alone.

2. Methods

2.1. Material

Solid waste from a full-scale chemi-thermo mechanical pulping of *Pinus radiata* wood was obtained from a wastewater treatment plant. This sludge contained wood fibres and other biological material. It was dewatered at the mill and the residue contained approximately 35% dry solids. The sludge was frozen until required.

2.2. Hydrothermal treatment

A well-mixed sub sample of sludge was mixed with tap water to form a slurry containing 3% total suspended solids (TSS). The slurry was kept at 4 °C and homogenised by means of a magnet stirrer at the start of each experiment.

Single runs of wet oxidation or thermal hydrolysis were carried out in a high temperature high pressure Parr reactor (4540 high pressure reactor equipped with a 4848 controller, Parr Instrument Company, USA). The reactor (Fig. 1) was equipped with a pre-heated feed tank in which 150 ml sludge was heated to 90 °C for 5 min with stirring to minimise the temperature gradient on transfer to the main reactor.

The reactor was initially charged with 150 ml water and pressurised to 20 bar with either pure oxygen (for wet oxidation) or nitrogen (for thermal hydrolysis). It was then heated to 220 °C before the pre-heated material was introduced by means of pressure difference. The initial concentration of solids in the reactor was approximately 1.5 wt%. The sampling tube was flushed with water followed by nitrogen before each sample was collected. Using a manual system 10 ml samples were taken during the 120 min reaction process. Samples were cooled immediately to stop further reaction. The $t = 0$ sample was prepared outside the reactor and its concentration was equivalent to that of the mixture in the reaction.

2.3. Analysis

Wood extractives were isolated using solvent extraction following the method of Robinson et al. (1999) which is suitable for pulp mill treatment system effluent and process water. The liquid samples were adjusted to pH 9 and then extracted using high purity