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Fast pyrolysis of low and high ash paper waste sludge: Influence of reactor temperature and pellet size

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ABSTRACT

Paper waste sludge (PWS) is a waste produced in large quantities by the pulp and paper industry, and is usually disposed by landfilling. This study investigates the pyrolytic conversion of PWS as an alternative to its valorisation. Low and high ash PWSs (8.5 and 46.7 wt%) were subjected to fast pyrolysis conversion to maximise the bio-oil yield by optimising the reactor temperature and pellet size. Maximum bio-oil yields of 44.5 ± 1.7 daf, wt% at 400 °C, and 59.9 ± 4.1 daf, wt% at 340 °C, for an intermediate pellet size of 4.84 ± 0.15 mm, were attained from the conversion of the low and high PWS, respectively. The low optimal reactor temperatures, as well as the high bio-oil yields, make valorisation via fast pyrolysis conversion promising. A significant reduction in the O/C molar ratio of up to 35%, from the high ash PWS to its bio-oil product, led to a 65% increase of the higher heating value. A thermogravimetric study was implemented to investigate the pyrolytic mechanisms behind the increase in bio-oil yield with intermediate pellets sizes. It revealed that the observed increase in non-condensable gas yield, which corresponded to a decrease in the bio-oil yield, was due to the promotion of exothermic reactions for high heating rates using smaller pellet sizes.

1. Introduction

The pulp and paper industry produces large quantities of paper waste sludge (PWS), which is composed of organic matter and has the potential to be used as a renewable energy source [1]. It is rejected for use in pulp and/or paper production due to the fibre length and quality being inadequate for the finished product. Typical quantities produced by pulp and paper mills are in the range of 60–100 kg and 50–600 kg per ton of final product, respectively, and is usually disposed of by landfilling [2]. Due to increasing costs and negative environmental impact of land filling, a more environmentally friendly alternative such as thermochemical conversion of PWS is required [3–6]. In this study, the process of pyrolysis, whereby the feedstock is thermally decomposed in the absence of oxygen, into the products of bio-oil, non-condensable gas and char, is used.

PWS varies in ash content (AC) depending on the type of mill (pulp or paper), and feedstock used. Paper mills that use recycled paper as a feedstock, typically produce PWS (deinking sludge) that is high in AC (~40 wt%) due to the removal of fillers such as calcium carbonate [3]. While pulp mills that use wood species as a feedstock, typically produce PWS that is low in AC (~6 wt%) [3]. The presence of ash is generally seen as a disadvantage in pyrolysis conversion as the yield of bio-oil is decreased. Thermogravimetric studies were performed on a range of different PWS types by Mendez et al. [3] to characterize their pyrolytic behaviour. Results indicated that the presence of high AC and degraded fibres, particularly in PWS from paper mills using recycled paper as a feedstock, lowered the starting temperature for weight loss [3]. This result pointed out the critical role of the ash content on the whole pyrolysis process. Recent studies by Strevoz and Evans [6] investigated the thermal characteristics and energy required for pyrolysis of recycle PWS with a low AC of 7.8 wt%. The samples were slowly pyrolysed (10 °C min^{-1}), in a packed bed thermal apparatus, to 700 °C offering a good compromise for the production of bio-oil (36 wt% or 43 daf, wt%), gas (31 wt%) and char (32 wt%). Lou et al. [4] subjected deinking sludge, with a high AC of 41.5 wt%, to thermogravimetry, Py–GC/MS and slow pyrolysis (fixed bed) to investigate its thermal characteristics.

Abbreviations: AC, Ash content; AL, Ash loss; BFBR, Bubbling fluidised bed reactor; CE, Conversion of energy; FP, Fast pyrolysis; FT-IR, Fourier transform infrared spectroscopy; HAPWS, High ash paper waste sludge; HHV, Higher heating value; LAPWS, Low ash paper waste sludge; MC_{Ca}, Calcium mass balance; PS, Pellet size; PWS, Paper waste sludge; RT, Reactor temperature; SDTA, Simultaneous differential thermal analysis; TGA, Thermogravimetric analysis; XRF, X-ray fluorescence.

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The slow pyrolysis experiment, performed at 800 °C, resulted in bio-oil, gas and char yields of 24.4 (41.7 daf, wt%), 28.8 and 45.8 wt%, respectively. In another study, Yang et al. [7] and Ouadi et al. [5] investigated the characteristics of bio-oil produced from intermediate pyrolysis of two different pelletized deinking sludges which were high in AC (62.9 and 74.5 wt%, respectively). Intermediate pyrolysis was performed on the deinking sludges using an Auger reactor at 450 °C under atmospheric pressure. The conditions of intermediate pyrolysis lie between those of fast and slow pyrolysis whereby feedstock residence times are long (7 to 10 min; slow pyrolysis), but vapour residence times are short (few seconds; fast pyrolysis) [7]. It was suggested by Yang et al. [8] that the heating rate is significantly lower than in fast pyrolysis. The product yields, reported by Yang et al. [7], for the bio-oil, char and gas yield were 10 (27.9 daf, wt%), 79 and 11 wt%, respectively. The bio-oil, with a higher heating value (HHV) of 36.5 MJ kg^{-1} and low oxygen content, was shown to supply sufficient heat to power a diesel engine [7]. Ouadi et al. [5] concluded that intermediate pyrolysis of PWS is a feasible method for its valorisation. This brief retrospect on pyrolysis of PWSs indicates that bio-oil yields vary in large extent depending on their origin and that the products offer a good potential energy source.

While fast pyrolysis technologies are known to enhance bio-oil yields [9], only slow and intermediate pyrolysis has been considered in all cases mentioned above. Typically the conversion of biomass via fast pyrolysis (FP), when compared to other techniques, offers the highest quantity, quality and energy content of bio-oil [10–13]. In this study, the FP of PWS is investigated in order to determine the potential of bio-oil as a high-energy feedstock. Indeed it is often mentioned that the production of bio-oil is favoured as it is easily handled, stored and is energy dense [10]. The FP conversion of biomass has been demonstrated to be a promising process for bio-energy production such as transportation fuels [10], thermal and electrical energy [10,13,14].

Therefore, the aim of this work focussed on the maximisation of the bio-oil from the FP conversion of low and high ash PWS, by optimising the reactor temperature and pellet size. This is performed using a 2-way linear and quadratic statistical model. In addition to that a thermogravimetric study was performed on different PWS pellet sizes at different heating rates to gain insight on the pyrolysis mechanisms.

2. Materials and methods

2.1. Raw materials and preparation

Two different PWS types were sourced based on the type of mill. The first type of PWS, which was particularly low in AC (8.5 wt% at 525 °C, Table 1), and was termed as low ash paper waste sludge (LAPWS), was supplied by the Kraft pulp mill, Sappi Ngodwana. The second type, which had a high AC (46.7 wt% at 525 °C, Table 1), and was termed as high ash paper waste sludge (HAPWS), was supplied by the recycle tissue paper mill, Kimberly Clark Enstra. The as-received wet LAPWS and HAPWS were dried in an oven for 12 h at 105 ± 2 °C. The dried sludge was then milled to separate the clumped fibres, using a 2 mm sieve on a Retsch hammer mill. The PWS was subsequently pelletized to improve feeding (screw fed) and fluidisation in the bubbling fluidised bed reactor. Initially the milled PWS was rehydrated (PWS:Water 1:1), and then pelletized using a Trespade No.12 electric meat mincer, after which the pellets were dried for 12 h at 105 ± 2 °C. The pellets were produced in sizes varying between 3 and 6 mm. All the pellet sizes were found to fluidise well in the bed.

Table 1
Physico-chemical characterisation of the LAPWS and HAPWS.

	LAPWS	HAPWS
Moisture content after drying (wt%)	80.9	54.6
Proximate Analysis (wt%, db)		
Volatile Matter	78.7	50.3
Fixed Carbon	15.5	2.9
Ash Content (900 °C)	5.8	24.6
Ash Content (525 °C)	8.5	46.7
HHV (MJ/kg)	17.8	12.1
Lignocellulosic Composition (daf, wt%)		
Extractives	6.3	10.5
Cellulose	58.7	49.5
Hemicelluloses	15.3	19.0
Lignin	20.1	20.5
Ultimate Analysis (daf, wt%)		
C	49.2	47.2
H	5.9	6.7
O (by difference)	44.8	45.7
N	0.08	0.41
S	0.00	0.00

2.2. Feedstock characterisation

2.2.1. Physico-chemical characterisation

The cone and quartering sub-sampling method (DD CEN/TS 14780:2005) was used on the LAPWS and HAPWS batches to select samples for physico-chemical characterization. The moisture content for the as-received PWS was determined in accordance with the TAPPI T264 om-88 standard procedure. Ash content (AC_{525}) was determined in accordance with the ISO 1762 standard procedure using a muffle furnace to combust the samples at 525 ± 5 °C. The mineral composition (oxides) of the PWS was determined via X-ray fluorescence (XRF) analysis using an AXIOS PANalytical. Fused glass discs were used for the major elemental analysis. Trace elemental ICP analysis was performed on the HAPWS to determine the calcium content. Samples (0.25 g) were initially digested by microwave using nitric acid (7 mL) after which 43 mL of deionised water was added. The digested samples where then subjected to ICP analysis using a Thermo Scientific iCap 6200 series spectrometer. The HAPWS was further subjected to Fourier transform infrared (FT-IR) spectroscopy to determine the form of the calcium components. This was performed using a PerkinElmer Paragon 1000PC FTIR spectrometer with a MTEC Photoacoustic Model 300 attachment. The resulting FT-IR spectra of the HAPWS feedstock was compared to those of pure compounds such as calcium carbonate, calcium hydroxide and calcium oxide (Edu Trade). Proximate analysis was determined for the LAPWS in accordance with the ASTM E1131 standard procedure using a TGA/DSC 1-LF1100 Mettler Toledo. In Section 3.1, the inorganic composition of the HAPWS was shown to be comprised mainly of calcium carbonate which thermally decomposes at temperatures above 650 °C [3] according to Eq. (1).

$$CaCO_3 \rightarrow CaO + CO_2 \quad (1)$$

Thus, the ASTM E1131 method was altered for HAPWS, by including a step holding the temperature at 650 °C for 5 min to drive off the organic volatiles, after which it was heated to 900 °C and held for an additional 5 min to insure full calcium carbonate decomposition occurred before combustion of the fixed carbon. The remaining ash, after combustion of the fixed carbon, was termed AC_{900}. Ultimate analysis was performed using a TruSpec Micro from LECO. During ultimate analysis samples are combusted in a fluidised bed at 1080 °C, thus making calcium carbonate decomposition into CO_2 (Eq. (1)) for HAPWS inevitable. To determine the organic carbon content the weight percentage of CO_2, produced by calcium car-