VALORISATION OF PAPER WASTE SLUDGE *VIA* FERMENTATION AND PYROLYSIS

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The pulp and paper industry produces large quantities of paper waste sludge (PWS), typically 100 to 500 kg PWS per ton of paper, usually disposed of by landfill. This material has a high organic content and can thus be used as a feedstock for fermentation and pyrolysis or a combination of the two processes. 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 ^{o}C, and 59.9 ± 4.1 daf, wt% at 340 ^{o}C, for an intermediate pellet size of 4.84 ± 0.15 mm, were attained from the conversion of the low and high PWS, respectively. A thermogravimetric study found 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. PWSs with low and medium ash content were utilized for the production of ethanol via simultaneous saccharification and fermentation. The two samples were screened for fermentation efficiency with different enzyme cocktails and yeast strains and found to vary significantly between different enzymes, but not between different yeast strains. The two samples were further investigated in a fed-batch culture, which indicated that medium ash PWS was a better feedstock for bioethanol production compared to low ash PWS. It is expected that the fermentation residue will be suitable for pyrolysis.

Keywords: fermentation, pyrolysis, paper waste sludge

INTRODUCTION

The pulp and paper industry produces large quantities of paper waste sludge, which is composed of organic matter, largely cellulose, and has the potential to be used as a renewable energy source.[1] Typical quantities produced by pulp and paper mills are in the range of 60 to 100 kg and 50 to 600 kg per ton of final product, respectively, the wastes being usually disposed of by landfill.[2] Given the high content of organic material, the potential for fermentation or pyrolysis has been investigated with a combination of the two processes, presenting an interesting biorefinery concept. To date, the focus of pyrolysis has been on the slow and intermediate options,[3,4] however fast pyrolysis technologies are known to enhance bio-oil yields.[5] 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.[6] Thus, the pyrolysis work has focused on maximisation of the bio-oil from FP conversion of low and high ash PWS, by optimising the reactor temperature and pellet size. In addition, a thermogravimetric study was performed on different PWS pellet sizes at different heating rates to gain insight on the pyrolysis mechanisms.

Paper waste sludge can also be used as a feedstock for fermentation. It can be utilized without pretreatment since the cellulose fibers are already accessible to enzymatic degradation due to the pulping process.[7] Fermentation typically results in the conversion of glucose and thus the fermentation residue will still contain organic material suitable for pyrolysis. PWS does, however, have several disadvantages, such as the high ash content, associated with mills recycling mainly printed material, and the high water holding capacity, associated with paper substrates. Large amounts of ash in PWS result in higher capital and material costs due to the requirement of larger vessels and larger amounts of enzymes, respectively.[8] The high water holding capacity of paper substrates makes it difficult to work with them and special agitators for semi-solid slurries are required.[9] Fed-batch fermentations are commonly used to achieve higher solid loadings and ethanol concentrations compared to batch fermentations, which consequently

result in processes that are more profitable.

EXPERIMENTAL

Raw materials, preparation and characterisation

Paper waste sludge samples were collected from three paper and pulp mills in South Africa. The first type of PWS, which had a low ash content (AC) (8.5 wt%, Table 1), was termed as low ash paper waste sludge (LAPWS), and was supplied by a Kraft pulp mill, Sappi Ngodwana. The second type had a high AC (46.7 wt%, Table 1), and was termed high ash paper waste sludge (HAPWS), and was supplied by a recycled tissue paper mill, Kimberly Clark Enstra. The third type of PWS had a medium AC (20.5 wt%, Table 1) and was termed medium ash paper waste sludge (MAPWS), and was supplied by a recycled corrugated cardboard mill, Mpact Springs. Proximate analysis was performed on the LAPWS and MAPWS in accordance with the ASTM E1131 method, using a Mettler-ToledoTGA/DSC 1-LF1100 system. However, for HAPWS this method was altered, as described in detail by Ridout *et al.*[10] The ash content was determined by combusting the LAPWS (525 ± 5 ^{o}C), HAPWS (525 ± 5 ^{o}C) and MAPWS (575 ± 5 ^{o}C) in a furnace. The LAPWS and HAPWS were used in the pyrolysis experiments and were subsequently pelletized to improve feeding and fluidisation.[10] The LAPWS and MAPWS were used in the fermentation experiments and were dried in a high tunnel at approximately 40 °C and kept in plastic bags until used in fermentations.

Fast pyrolysis experiments

The experiments were carried out using a fast pyrolysis unit with a feed capacity of 0.5 kg.h^{-1}.[13]The set-up had four main sections, namely feeding, bubbling fluidised bed reactor (BFBR), char separation and liquid condensation. The fast pyrolysis bio-oil yields were calculated based on a dry ash free basis and is represented by Equation 1:

$$Y_{bio\text{ - }oil}\,(\text{daf wt.\%}) = \frac{M_{bulk\text{-}liquid} + M_{tarry\text{-}phase} - M_{ash-oil}}{M_{PWS} - M_{ash-pws} - M_{moisture}} * 100 \quad (1)$$

where M is the mass of products in grams, and $M_{moisture}$ is the moisture contained in the PWS. The difference in weight of the liquid condensation train equipment (bio-oil residue), before and after each pyrolysis run, as well as the bio-oil recovered from the reservoir formed the bulk liquid ($M_{bulk\text{-}liquid}$). The bulk liquid along with the tarry phase, $M_{tarry\text{-}phase}$, recovered from acetone washing of the internal reservoir walls, forms the total bio-oil mass.

Fast pyrolysis design of experiments

A three-level two-factor full factorial statistical design was implemented to optimise the reactor temperature and pellet size for maximization of the bio-oil yield from fast pyrolysis of the PWS. From pre-screening fast pyrolysis runs, the appropriate reactor temperature levels of 300, 425 and 550 ^{o}C for LAPWS, and 290, 340 and 390 ^{o}C for HAPWS were selected. Particle size is known to influence the heat and mass transfer effects during pyrolysis.[15-17] Pellet size was considered as a single particle with pellet sizes in the range of 2.92 ± 0.12, 4.04 ± 0.18 and 4.84 ± 0.15 mm. An ANOVA analysis was performed using the parametric data analysis function 'regression' in Microsoft Excel (2010, ver. 14.0.7128.5000, SP2), whereby a 2-way linear and quadratic model was fitted (Equation 2):

$$Y_{product}\,(\text{wt.\%}) = \text{intercept} + \beta_1 * RT + \beta_2 * PS + \beta_3 * RT^2 + \beta_4 * PS^2 + \beta_5 * RT * PS + \beta_6 * RT^2 * PS + \beta_7 * PS^2 * RT + \beta_8 * RT^2 * PS^2 \quad (2)$$

where $Y_{product}$ is the pyrolysis product yield, $\beta_{n+1}$are model coefficients, RT is the reactor temperature (^{o}C) and PS is the pellet size (mm).

Table 1
Proximate composition of low, medium and high ash paper waste sludge

	Proximate analysis (wt%, db)				
PWS type	VM	FC	AC (900 ^{o}C)	AC (wt%, db; 525 ^{o}C)	Ref.
LAPWS	78.7	15.5	5.8	8.5	10
MAPWS	76.1	6.8	17.1	20.5[a]	-
HAPWS	50.3	2.9	24.6	46.7	10

VM: Volatile matter; FC: Fixed carbon; AC: Ash content; [a]determined at 575 ^{o}C

Batch and fed-batch fermentations

Batch and fed-batch fermentations were carried out in 100 mL Erlenmeyer shake flasks and 5 L bio-reactors, respectively. Optiflow RC 2.0, Spezyme CP and AlternaFuel CMAX were used as enzymes with Novozym 188 as β-glucosidase in a 10:1 ratio, together with *Saccharomyces cerevisiae* MH1000, TMB3400 and D5A as the microorganisms. The nutrient medium was as described by Kadam *et al.*[11]: inoculation volume 5% (v/v) and the reactions were maintained at 37 ^{o}C for 168 h. Batch fermentations were done at a solid loading of 20 g.L^{-1} and fed-batch fermentations were done with 3wt% initial solid loading with 3 wt% feedings every 12 h. Samples were taken every 24 h and analyzed for ethanol concentration.

Fermentation analytical methods

Glucose concentrations (for theoretical ethanol yield calculations) were determined by acid hydrolysis of 70% H_2SO_4 and measured together with ethanol concentration by high performance liquid chromatography (HPLC).

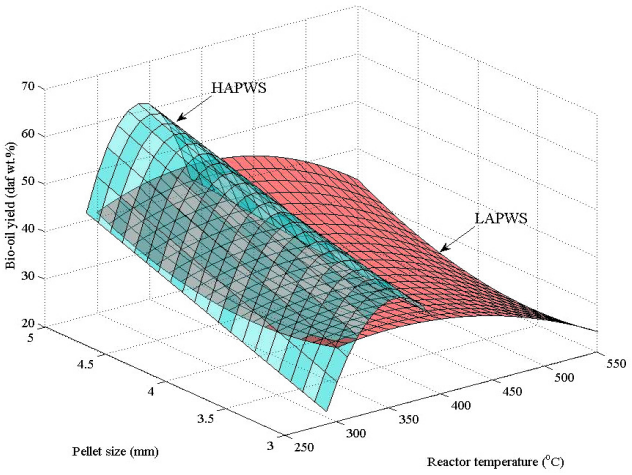

Figure 1: Evolution of bio-oil product yields (daf, wt%) from fast pyrolysis conversion of LAPWS and HAPWS for different reactor temperatures and pellet sizes (modified and redrawn from Ridout*et al.*[13])

RESULTS AND DISCUSSION

Pyrolysis of PWS

Trends in the LAPWS and HAPWS fast pyrolysis bio-oil yield surface plots are presented in Figure 1. Optimal reactor temperatures for maximisation of the bio-oil yields were attained at 400 °C and 340 °C for LAPWS and HAPWS, respectively, and are significantly lower when compared to optima for other lignocellulosic biomass (450 to 550 °C).[12] These low temperatures could be due to the catalytic effect of calcium, which is present in large quantities,[10] promoting primary pyrolysis reactions.[13] An additional run was performed using an elevated pellet size of ~6mm at the PWS optimum reactor temperatures, which resulted in a decrease in the bio-oil yield, confirming an optimum pellet size range between 4.84 ± 0.15 and ~6 mm.[10] At the pellet size of 4.84 ± 0.15 mm and optimal reactor temperatures, maximum bio-oil yields of 44.5 ± 1.7 and 59.9 ± 4.1 daf, wt% were attained for LAPWS and HAPWS, respectively (Figure 1).

Typically, the use of small particle sizes enhances the production of bio-oil during fast pyrolysis by allowing for a more predominant chemical kinetic regime.[12-14] If this latter statement can be applied to the influence of the pellet size on the bio-oil yield, the above mentioned results contradict those reported in the literature, as higher bio-oil yields were attained with an intermediate pellet size. To gain insight into the mechanisms involved during the conversion of pelletized PWS, a thermogravimetric study was implemented to illustrate the potential mass and heat transfer mechanisms on pyrolysis. Heat flux curves during the pyrolysis of LAPWS and HAPWS were recorded using TGA under low (20 °C.min^{-1}) and high (150 °C.min^{-1}) heating rates. Subsequently, it was 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.[10]

Fermentation of PWS

The medium and low ash paper waste sludges were chosen for ethanol production rather than the HAPWS due to the negative effect of high ash content on the fermentation process. There was no significant difference in the ethanol concentration obtained from MAPWS and LAPWS for the various yeast strains. However, the ethanol concentration for the two samples with the various enzyme cocktails was significantly different, with Optiflow RC 2.0 an almost three times higherethanol concentration was obtainedthan with AlternaFuel CMAX. The yeast strain MH1000 and the enzyme Optiflow RC 2.0 were chosen for further optimization in the fed-batch culture. In the fed-batch culture, the maximum solid loading possible for each of the

PWS types was investigated at constant enzyme dosages. Higher solid loadings are needed to have more cellulose available for conversion into ethanol. Enzymes are expensive and contribute significantly to the operating cost of a bioethanol plant. Therefore, an enzyme dosage of 10 $FPU.gds^{-1}$ was chosen. The maximum solid loading possible was 33 wt% for MAPWS and 12 wt% for LAPWS. An ethanol concentration of 49.2 and 12.4 $g.L^{-1}$, and yield of 69 and 39% of the theoretical maximum, were obtained for MAPWS and LAPWS, respectively. The significantly higher solid loading of MAPWS increased the amount of cellulose available for fermentation, and resulted in a significantly higher ethanol concentration.

CONCLUSION

The valorization of PWS into energy dense bio-oil products *via* fast pyrolysis offers a promising alternative, giving bio-oil yields of up to 44.5 ± 1.7 (400 ^{o}C at 4.84 ± 0.15 mm) and 59.9 ± 4.1 daf, wt% (340 ^{o}C at 4.84 ± 0.15 mm), at low temperatures, for LAPWS and HAPWS, respectively. Medium ash PWS resulted in maximum ethanol concentrations of 49.2 $g.L^{-1}$ at a solid loading of 33 wt%, compared to an ethanol concentration of 12.4 $g.L^{-1}$ achieved by low ash PWS at a maximum solid loading of 12 wt%. The higher ethanol concentration and yield obtained by MAPWS indicates that it is a better feedstock for ethanol production. The fermentation residue from the optimised process will be investigated for its potential as a pyrolysis feedstock to produce additional energy products.

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