



Physicochemical Characteristics of Different Pulp and Paper Mill Waste Streams for Hydrothermal Conversion

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The pulp and paper industry generates significant amounts of waste from various processes consisting of organic and inorganic matter. Due to its composition, the management of pulp and paper mill sludge presents an economic burden for wastewater treatment plants. In South Africa, paper mill sludge is mainly incinerated, landfilled or used for land application. These practices cause environmental and health hazards. In this study, a process of stabilization of paper mill sludge through hydrothermal carbonization is proposed. The quality of biochar produced and energy yield will depend on the elemental composition, calorific value and ash content of the sludge. Results revealed samples are composed of flat fibrous cellulosic morphology, with high volatile matter and little fixed carbon percentage. The main decomposition occurred between 220-400 °C. Sludge from primary clarifier contains the highest ash percentage, hence it was found to be unsuitable for energy recovery through hydrothermal carbonization. Sludge from kraft and recycling paper mills exhibited lower ash content and higher caloric values, thus more preferable for coal conversion through hydrothermal carbonization. The sludges have a sulfur composition (2.33%) compared to heavy fuel oils and bituminous coal.

1. Introduction

In the pulp and paper industry, waste residues are generated from primary clarifiers, biological treatment, and recycling paper streams (Kaur et al., 2020). The composition of pulp sludge and solid residues recovered from the waste stream depends on the origin of the cellulose fiber (wood or recycled paper). In general, sludge from pulp and paper mills is composed of water, organic material (mainly wood fiber such as cellulose) and inorganic compounds such as calcium carbonate (Méndez et al., 2009). Primary sludge consists of higher solid residues and lower inherent moisture compared to secondary sludge (Kaur et al., 2020). Sludge from recycling paper mills is composed of impurities such as lumps of fibers, staples and metals, sand, glass and plastics (Méndez et al., 2009). Due to high moisture content and poor dewatering properties, the management of pulp and paper mill sludge requires major investment and operating costs.

In South Africa, the pulp and paper mills are estimated to generate 0.5 million tonnes of sludge annually (Boshoff et al., 2016), which is commonly disposed of through incineration, landfilling, or land-farming applications. Sludge incineration results in the emission of Greenhouse Gases (GHG), and non-methane volatile compounds such as nitrogen dioxide (NO₂) and sulphur dioxide (SO₂) into the atmosphere, which are major persecutors of acid rain and have a negative impact on the environment and human health (Majewski and Jääskeläinen, 2004). Landfilling and land-farming also raise serious environmental concerns due to unmitigated leaching of toxic substances used in the pulping industry from the sludge into the ground. Additionally, the increasing demand for recyclable materials such as paper has resulted in an ever-increasing amount of waste fiber thereby posing a major challenge in landfilling capacity. Hence, implementing alternatives to divert sludge from landfill sites will alleviate costs associated with sludge management and reduce GHG emissions.

The carbon content in pulp and paper mill sludge is technically and economically feasible to recycle (Campbell, 2000). However, due to its inherent moisture, active drying of the feedstock is required before most thermochemical conversion processes (Zhao et al., 2016). Hydrothermal carbonization (HTC) makes the use of

biomass with high moisture content and converts it into solid coal-like product, referred to as “hydrochar” (Funke and Ziegler, 2010). It seems feasible for upgrading wet, low-value fuels by lowering the oxygen and volatile contents which consequently increases the energy density and improves the hydrophobic properties (Funke and Ziegler, 2010, Libra et al., 2011). The presence of high ash content in the feedstock is undesirable for thermochemical conversion. High ash percentages decrease the gross calorific of a fuel material (Lieskovský et al., 2017) which consequently results in poor combustion properties. In addition, high ash affects the technical design of a processing plant as it often leads to metal corrosion, operating problems during combustion and requires further disposal of residues (Wang et al., 2020a).

Thus, this study aims to assess the elemental composition, calorific values, ash content, and combustion behavior of sludge from different pulp and paper mill operations for the selection of the most feasible feedstock for valorization through HTC process.

2. Materials and methods

2.1 Materials

Sludge generated from raw pulping process, primary clarifier and recycling process, were collected from two different operating mills in South Africa which produce approximately 6,000-20,000 tonnes per year on a dry basis. The samples were collected in a closed container and stored in a cold room for analysis.

2.2 Experimental methods

The obtained samples were dried in an oven at 80 °C for 24 hours to minimize the effect of inherent moisture. The dried samples were ground and sieved to a particle size less than 250 µm prior to further characterization.

2.2.1 Scanning electron microscopy (SEM)

The dried and sieved samples were mounted on an aluminum plate using a double-sided carbon adhesive tape and coated with films of carbon using Quorum Q150T ES. Scanning electron microscopy (SEM) using FEG SEM (Zeiss Gemini 2 Crossbeam 540) to analyze the surface morphology of the samples. The working distance (WD) was between 2.6-2.7 mm, with magnification from 750-1200 X at a voltage (EHT) of 1 kV. Samples for analysis on SEM were prepared following the procedure described in Aliakbarian (2017).

2.2.2 Proximate Analysis

The residual moisture, volatile matter (VM), fixed carbon (FC) and ash content were analyzed using a thermogravimetric analyzer (Hitachi STA300 TGA-DTA) according to the ASTM D7582-15 test standard. For residual moisture determination, the sludge samples with known weight were placed in crucibles without covers and heated at a heating rate of 20 °C/min from room temperature to 107 °C, followed by 107°C isothermal hold for 1 h under nitrogen atmosphere at a flow rate of 80 mL/min. The difference in the weight before and after drying indicates the residual moisture. The total moisture content percentage was calculated according to the equation below:

$$MC = \{M_{AD} + [(1 - M_{AD}) \cdot M_R]\} \cdot 100 \quad (1)$$

Where MC is the total moisture content, M_{AD} is the moisture recorded after drying the sample for 24 hours, M_R is the residual moisture.

For volatile matter, a heating ramp (40 °C/min) was programmed to 950 °C, followed by an isothermal hold of 7 min under nitrogen atmosphere at a flow rate of 80 mL/min. The weight difference prior and after the ramp was recorded. For ash determination, the furnace was cooled from 950 to 600 °C at a cooling rate of -40 °C/min. The flowing gas was changed to oxidizing gas (air) at 80 mL/min, and the final temperature was raised to 750 °C within 1 h. Similar to residual moisture and volatile matter, the weight difference showed the ash content. Finally, the fixed carbon content was determined by subtracting the percentage values obtained for residual moisture, volatile matter and ash content from 100%.

2.2.3 Elemental composition

Elemental analysis of carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) content was conducted using a Flash 2000 Elemental Analyzer (Thermo Fisher Scientific). Approximately 2 mg of each sample was used per analysis. The composition of CHNS was recorded and the oxygen content was calculated using equation 2:

$$0\% = 100\% - C\% - H\% - N\% - S\% - \text{Ash} \quad (2)$$

2.2.4 Energy content

The calorific values, based on higher heating value (HHV) of the samples dried in an oven at 80 °C for 24 h were analyzed using a bomb calorimeter (Parr 6200 Oxygen Bomb Calorimeter). About 250 mg of the dried of each sample with particle size less than 250 μm was placed in a crucible and transferred to the vessel. For optimum combustion, the vessel was pressurized with oxygen to 3000 kPa, and placed in the chamber. The sample was combusted in the vessel, and the energy released by the combustion (observed by water temperature increase) was measured. The lower heating value (LHV) was calculated based on the higher heating value obtained from the calorimeter, hydrogen content from the elemental analysis and residual moisture content.

2.2.5 Thermogravimetric analysis

The decomposition behavior of the samples was analyzed by thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) with a thermogravimetric analyzer (Hitachi STA300 TGA-DTA). About 10 mg of each sample was placed in a crucible and heated under air atmosphere and heated to 1000 °C at a flow rate of 80 mL/min. The weight loss and the corresponding weight loss rate (DTG) of the samples were measured continuously under non-isothermal conditions at a constant heating rate of 20 °C/min.

3. Results and discussion

The SEM images are reported in Figure 1. All samples presented fibrous morphology consisting of flat cellulose fibers longer than 100 μm and width varying from 23-53 μm, with recycling paper sludge (RPS) consisting of the widest fibers. Fibers from raw sludge (RS) and primary clarifier (PS) showed a relatively smoother surface, however, RS exhibited a larger number of microscopic holes per area and cleaner surface. RPS showed higher degradation of fibers which can be observed by the rough irregularities in surface texture (rough and smooth) and width, as well as aggregates of inorganic particles. PS consisted of a higher content of inorganic fillers such as calcium carbonate, a by-product in the causticizing process of the kraft pulping process, as well as chemical dissolved in water during pulping, paper making and wastewater primary treatment. This is further confirmed by the ash percentage in Table 2.

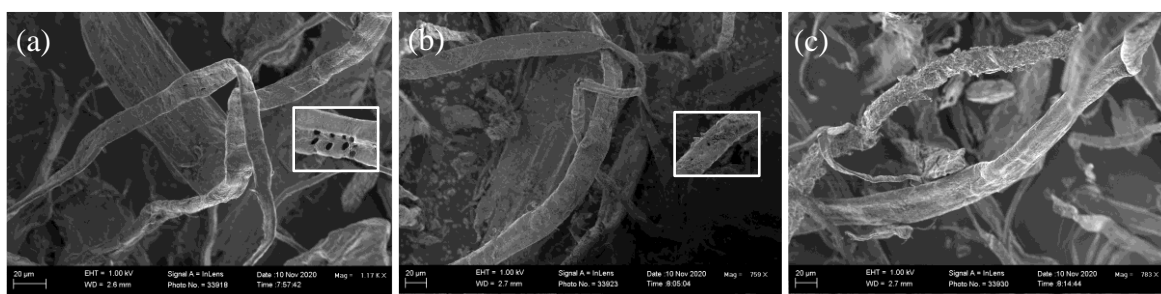


Figure 1: SEM images of (a) raw sludge, (b) primary sludge and (c) recycled paper sludge.

The total moisture content and calorific values are reported in Table 1. The total moisture percentages include the residual moisture of the samples from the proximate analysis. Moisture content is of great importance for the energetic use of fuel material. Sludges containing 30% to 50% moisture are undesirable for thermal processes such as incineration, pyrolysis and gasification. This is because the presence of water substantially affects the calorific value of the fuel. In the case of incineration, the temperature for combustion must be 10 °C higher for each additional 1% of water content in sludge (Likon and Trebe, 2012). The percentage of moisture content for PS was the lowest at 17.50%, and the highest was for RPS (36.46%). RS has relatively low moisture in comparison to RPS (25.10%), but they present similar characteristics in terms of energy content and elemental composition (Table 2 and 3).

The calorific values based on the higher heating value (HHV) and lower heating value (LHV) on a dry basis are also reported. HHV represents the total amount of heat present in the fuel including the latent heat of water

vaporization in the fuels and exhaust gas (Cai et al., 2017). LHV excludes the latent heat of vaporization, hence LHV is relatively lower than HHV. The calorific values reported were converted to a dry basis. PS was found to have lower HHV and LHV (9.79 MJ/kg and 8.90 MJ/kg, respectively) and compared to RS and RPS. The overall low calorific values of the samples may be attributed to high moisture percentages, for PS however is also due to high ash content, as reported in Table 2.

Table 1: Total moisture, higher heating values (HHV) and lower heating values (LHV) of raw sludge (RS), primary sludge (PS) and recycled paper sludge (RPS).

Sample	Total Moisture (% wt.)	Higher Heating Value (MJ/kg)	Lower Heating Value (MJ/kg)
RS	25.10	15.26	13.99
PS	17.50	9.79	8.90
RPS	36.46	15.33	14.00

Data on proximate analysis of fuel are important for evaluation of its potential for energy generation. Results of residual moisture, volatile matter, fixed carbon and ash are presented in Table 2. Although samples were dried in an oven at 80 °C for 48 hours, the proximate analysis was not performed immediately, thus the samples absorbed moisture from the environment. The residual moisture obtained in Table 2 is consistent with the combustion analysis in Figure 2. PS absorbed lower moisture (3.85%) and compared to RS and RPS (5.21 and 6.01, respectively). In general, the fixed carbon percentage on all samples exhibited a very low percentage of fixed carbon, however, the volatile matter percentage was significantly higher. The highest volatile matter was observed on RFS and RF at 77.15% and 76.01%, respectively.

Ash content, the inorganic residue remaining after the burning of the fuel, is an important parameter to consider when dealing with thermo-chemical processes. Pulp and paper sludge ash consists of mineral and inorganic components from raw material preparation, pulp making, fiber recycling, paper manufacturing and wastewater treatment operations. This is consistent with findings from recent studies on wood products as feedstock for proposed biorefineries (Zambare and Christopher, 2020). PS exhibited a high level of ash (31.51%). This is due to higher presence of non-combustible matter in the sludge. Apart from contributing to the poor calorific properties of the fuel material, a high level of ash affects the technical design of a processing plant as it often leads to metal corrosion, operating problems during combustion and requires further disposal of residues (Wang et al., 2020a). Depending on the melting point, high ash may lead to clogging of burners during incineration, as well as flame suffocation due to the deposition of ash in the vicinity of the burner. Thus, RS and RFS are more preferable for thermochemical conversion due to the relatively lower ash content. This will also help to minimize accumulation sintering and agglomerations in boilers, which often leads to failure of the plant.

Table 2: Results from proximate analysis (weight percentage).

Sample	Residual Moisture	Volatile Matter (% d.b)	Fixed Carbon (% d.b.)	Ash (% d.b.)
RS	5.21	76.01	10.13	13.87
PS	3.85	63.31	5.18	31.51
RPS	6.01	77.15	10.59	12.26

The levels of carbon, hydrogen, oxygen, and sulphur from the ultimate analysis are reported in Table 3. All values were converted to a dry basis. The ash content used to estimate the oxygen in samples was assumed to be the same as the ones obtained from the proximate analysis. Samples exhibited reasonable levels of carbons (28.04-39.29%), which can be used as a source of energy. RS and RPS reported nearly the same ultimate analysis, while PS showed some difference in terms of carbon, hydrogen and oxygen. Generally, very little hydrogen was detected, but the concentration of oxygen was relatively higher, which contributed to the poor combustion properties of the samples. No nitrogen was detected during elemental analysis; therefore, samples present no risk of emissions of NO_x gases when incinerated. All samples exhibited similar sulphur composition (average of 2.33%) which is higher than the values reported in literature (Kaur et al., 2020, Scott, 1995). The sulphur content of the samples is similar to those of heavy fuel oils and bituminous coal, which normally ranges from 2-3% (Kaiser, 1968). When used as feedstock for hydrothermal conversion, in particular HTC, 90% of the sulphur may remain in solid fuels (Wang et al., 2020b). During combustion, the sulphur from these fuels leads to the emissions of SO₂ and SO₃, which are persecutors of acid rain. Traces of sulphur may also be present in incinerator fly ash, incinerator ash dumps and incinerators wall lags (Kaiser, 1968). Thus, it

is important to take steps to reduce sulphur concentration of the samples when using as feedstock for fuel conversion.

Table 3: Carbon (C), Hydrogen (H), Oxygen (O) and Sulphur (S) weight percentages per sample on dry basis.

Sample	C (%)	H (%)	O (%)	S (%)	Ash (%)
RS	39.29	5.12	39.47	2.27	13.87
PS	28.04	3.57	34.55	2.34	31.51
RPS	39.28	5.30	40.79	2.37	12.26

The thermogravimetric analysis (TGA) is a valuable technique used to assess the combustion properties of fuel materials. The decomposition behavior, represented by the TGA-DTG curves, are of utmost importance to determine the thermal reactivity and decomposition stages resulting from the increase in temperature. The TGA-DTG profiles of RS, PS, RPS are illustrated in Figure 2.

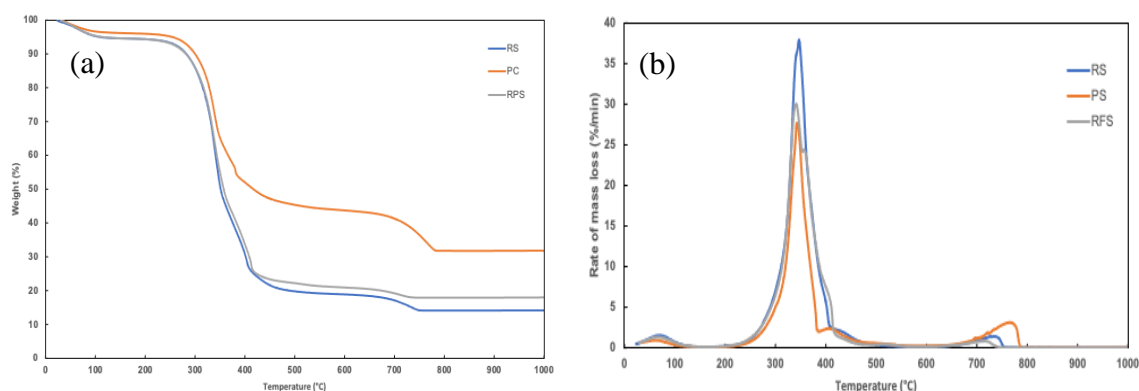


Figure 2: (a) Thermogravimetric analysis (TGA) and (b) derivative thermogravimetric (DTG) profiles of RS, PS and RPS.

The thermal decomposition of the samples involved several stages. The first stage was dehydration, which occurred between 29 °C to 117 °C and is illustrated by the small peak at about 73 °C, 62 °C and 68 °C on the DTG profile (Figure 2.b) for RS, PS and RPS, respectively. This corresponds to the residual moisture of the samples which is consistent with the proximate analysis. Followed by dehydration, the samples exhibited the main stage between 220 °C and roughly 400 °C, corresponding to a maximum peak at approximately 350 °C for both RS and PS, and 345 °C for RFS. The maximum weight loss for RS, PS and RPS observed at the second stage were about 35 %/min, 26 %/min and 29 %/min, respectively. This is attributed to the release of volatile matter associated with the decomposition of hemicellulose and cellulose component. Hemicellulose and cellulose peak temperatures of RS and RPS are slightly higher than those of PS. Peaks occurring at a temperature higher than 400 °C are attributed to the degradation of lignin. The typical composition of hemicellulose, cellulose and lignin in pulp and paper sludge is given in Table 4. Decomposition at peaks higher than 600 °C may be due to further degradation of lignin as well as degradation of volatile inorganic compounds and further oxidation of organic compounds.

Table 4: lignocellulose composition in different pulp and paper mill sludge (%wt) (R. Kaur, (2020).

Stage	Hemicellulose	Cellulose	Lignin
Primary	4.9-14.2	23.6-60.8	2.2-20.92
Secondary	12.0-15.0	2.0-28	16.85-58.0
Deinking	10.7-14.3	46-48.8	5.5-29.5

Based on the physicochemical characteristics data obtained in this study, the subsequent work will consist of designing of low-cost batch laboratory hydrothermal carbonization reactor to investigate the potential of the HTC process to address problems associated with pulp and paper mill sludge management in South Africa, by upgrading the sludge into solid fuel with enhanced combustion properties, as well as to determine the optimum HTC operating conditions to produce hydrochar from PS and RFS of maximal solid yield and calorific value.

4. Conclusions

Physicochemical characterization was performed on sludge from kraft pulping, primary clarifier and recycling paper stream to determine their feasibility for hydrothermal carbonization conversion. All samples consist of flat fibrous morphology, high volatile content and little fixed carbon percentage. The main lignocellulosic decomposition occurred between 220-400 °C. Sludge from the primary clarifier is not suitable for energy recovery through hydrothermal carbonization due to the high ash content. The presence of high ash contributes to the poor combustion properties of the fuel samples, affects the technical design and operation of the plant and has negative impact on the environment. Sludge from kraft and recycling paper mills have relatively low ash content, high caloric values (14 MJ/kg), and high moisture (25.10-36.46%), therefore they are more preferable for coal conversion through hydrothermal carbonization. The sulfur composition is similar for all samples (2.33% average) and is compared to heavy fuel oils and bituminous coal. Thus, measures need to be taken to decrease the high sulfur concentration in fuel samples when using as feedstock for fuel conversion.

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