Energy Recovery by Fast Pyrolysis of Pre-treated Trommel Fines Derived from a UK-based MSW Material Recycling Facility

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Abstract

In this experimental study, a physically pre-treated trommel fines feedstock, containing 44 wt% non-volatiles (ash and fixed carbon) and 56 wt% volatile matter (dry basis), was subjected to fast pyrolysis to recover energy from its organic load, using a 300 g h^{-1} bubbling fluidized bed (BFB) fast pyrolysis rig. A physical pre-treatment method (including crushing, grinding and sieving) was used to prepare a 0.5 – 2 mm sized trommel fines feedstock to make it suitable for fast pyrolysis in the BFB reactor. Experimental results from the fast pyrolysis process showed that the highest yield of organic liquid was obtained at around a temperature of 500 °C. However, both char and gas yields increased dramatically at temperatures above 500 °C, as a result of enhanced cracking of liquid components, which reduced the yield of liquid products. Overall, energy recovery from the pyrolysis products (liquid and gas products as well as char pot residues) ranged from 63 – 70 %, generally increasing with temperature. A large proportion of the high ash content (36 wt%) of the feedstock was found in the char pot (>62%), while smaller proportions were found in the reactor bed and some liquid products. The char pot ash residues composed mostly of non-hazardous earth materials and may be applied in bulk construction materials e.g. cement manufacture. Although, there was no problem with the pyrolysis rig during 1 hour of operation, longer periods of operation would require periodic removal of accumulated solid residues and/or char pot modification to ensure continuous rig operation and process safety.

Keywords: pre-treated trommel fines, fast pyrolysis, energy recovery, pyrolysis liquid, solid residues

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1 Introduction

Trommel fines are a by-product obtained from the mechanical recycling process of municipal solid waste (MSW). Landfill sites have been the traditional home for trommel fines, however with the increase in landfill taxes and the amendment of the Landfill Tax Regulation, processors are being forced to find alternative methods of handling trommel fines. The introduction of the Loss on Ignition (LOI) test in April 2015 now requires UK-based waste processors to ensure that LOI of trommel fines be less than 10% in order to be considered eligible for the lower rate of tax (HMRC, 2014). In other words, lower LOI values indicate lower calorific values. The solution is inevitable; waste processors must introduce methods for trommel fines clean up to remove the calorific materials e.g. through energy recovery, in order to reduce landfill tax bills. Energy recovery from trommel fines is a new frontier and big questions arise as to what technologies would be suitable for this type of waste.

A detailed analysis of the organic composition of trommel fines (Eke, Onwudili and Bridgwater, 2017), showed that they contained different biodegradable and non-biodegradable materials such as wood, stones, glass, ash, textiles, plastics, paper, cardboard, food waste and fibre. The HMRC estimates that the UK produces about 4.5 million tonnes of trommel fines each year (HMRC, 2014), representing just over 2 wt% of total annual waste generation. This mixed composition means that trommel fines could be likened to a mixed stream of MSW, for which biological technologies such as anaerobic digestion would not be suitable to eliminate the organic load. In contrast, thermochemical processes are usually faster and more robust than biological processes for mixed waste streams. For example, thermochemical processing can handle both biodegradable and non-biodegradable waste, whereas biological processing can only handle readily biodegradable waste (McKendry, 2002).

MSW pyrolysis can be considered as an innovative process for the pre-treatment MSW to obtain cleaner energy carriers and chemicals (Schaefer, 1975; Malkow, 2004), than the original feedstock. Indeed, pyrolysis gives intermediate products including gases and liquids, which have better handling properties, suitable for downstream processing to more valuable products than the original solid feedstock. Such downstream processing routes may include a more controllable gasification process to convert the pyrolysis vapour into syngas or isolation of high value chemicals from the condensed pyrolysis oil. In comparison, conventional MSW mass-burn incineration process gives heat as the main product, thereby foreclosing the potential for chemical added value. Additionally, the inert atmosphere used during pyrolysis leads to lower emissions of nitrogen oxides (NOx) and sulphur oxides (SO_2).

Numerous studies have been performed in laboratories to determine pyrolysis behaviours and product properties of MSW and individual MSW fractions such as paper, sewage sludge, plastics, fabric, lignocellulosic materials, refuse derived fuel (RDF) and RDF pellets (Grammelis et al., 2009; Bosmans et al., 2013; Zhao et al., 2011; Ates et al., 2013; Miskolczi et al., 2013). The interactions between the different individual fractions and the pyrolysis products have also been explored (Sørum et al., 2001; Grieco and Baldi, 2012). Among the listed feedstocks investigated for pyrolysis, RDF, sewage sludge and manures are known to have significant ash contents. High ash contents pose operational problems during thermochemical processing of wastes and can have significant effects on both the design and operability of reactors. For example, accumulation of ash, stones and pieces of concrete in beds of fast pyrolysis reactors can lead to hardware issues as well as rapid attrition of bed material, leading to entrainment of small particles in gas flows, with consequent dust deposition on downstream systems. In some cases, certain ash compounds, may be beneficial in terms the chemistry of pyrolysis. For instance, some ash compounds may serve as catalyst for the cracking of pyrolysis vapours, leading to the production of more valuable liquid and gaseous products (Pradhan, 2015; Renkonen, 2016).

Therefore, this research has been carried out in an attempt to provide baseline data on the technical feasibility of applying a 300 g h^{-1} bubbling fluidized bed fast pyrolysis system on trommel fines from a UK-based waste recycling facility, which contained a very high ash content. In this present work, fast pyrolysis of a physically pre-treated trommel fines feedstock was investigated in relation to reaction temperature, as a means of recovering energy from this type of problem waste. The aim was to reduce organic load of the feedstock, while leaving an inert solid for final disposal at a reduced landfill cost due to lower LOI or for potential useful application. Detailed analyses and characterisation of the pyrolysis products were carried out to determine the yields and compositions of gaseous and liquid products, as well as the fate of the ash during the fast pyrolysis process in order to draw up possible conclusions.

2 Experimental methods

2.1. Trommel fines feedstock

The sample used in this study was supplied by a UK commercial waste management company – Biffa Ltd from Leicester. The sample constituted the <10 mm-sized mixed particles left after mechanical sorting and trommel screening of household, thereby qualifying as trommel fines (Fitzgerald, 2013; Pitchell, 2014). The estimated percentage composition of materials in the trommel fines, carried out by visual inspection and hand separation, are given in Table 1. The sample was initially prepared to meet the feeding requirements of an existing bubbling fluidized bed fast pyrolysis reactor. Details of the pre-treatment procedure have been recently published (Eke, Onwudili and Bridgwater, 2017). In brief, the preparation method involved manual removal of visible large stones, glasses and concrete, followed by grinding with a Retsch Ltd., Germany, Heavy-Duty Cutting Mill, Knife Mill Type SM2000 and sieving to obtain a 0.5 - 2 mm size fraction. This fraction accounted for over 70 wt% of the original trommel fines feedstock, which comprised of mostly paper pellets, plastics, glass, stones, bones, miscellaneous wood, textiles and metals (Eke, Onwudili and Bridgwater, 2017). Table 2 summarises their main characteristics of this size fraction, which shows that it contained approximately 56 wt% of volatile matter, from which liquid and gaseous products could be obtained.

2.2 Fast pyrolysis experiments

Fast pyrolysis experiments were conducted in a bench-scale (300 g h^{-1} throughput) fluidized bed reactor unit shown in Figure 1 (Onwudili and Eke, 2019). Briefly, it consisted of a feeder, a reactor and a product collection system. The feeder consisted of a tubular storage hopper with a dual screw gravimetric feeding system with variable speed motor for feeding, attached to a fast screw. The pyrolysis occurred in a steel tubular reactor with an internal diameter of 41 mm and a height of 320 mm. It was filled with approximately 150 g of sand with particle size range of 500 – 600 µm as bed material for fluidization and heat transfer. The product collection system was composed of a water condenser, two dry ice/acetone condensers and a cotton wool filter.

For each experiment, fluidisation of the bed material was achieved by using inert nitrogen at a flow rate of approximately 6 L min^{-1}. At the start, the nitrogen gas, preheated to 250 °C, was used to remove air within the system for 10 min, followed by preheating the reactor using an electrical furnace. Preliminary tests showed that to achieve the desired reactor temperature of between 400 – 700 °C, the heater needed to be set 50 °C higher than the reactor temperature, due to the endothermic nature of the pyrolysis reactions. Throughout the experiments, temperatures were controlled within 6.5% of the set value. Once the temperatures of the fluidising medium reached a steady state, trommel fines in the feeder were continuously delivered into the reactor at the middle of the fluidised bed by nitrogen entrained flow via the air-cooled feeding tube. In this work, actual feeding rate ranged from 120 to 220 g h^{-1} and each experiment lasted for 60 min. The pyrolysis temperature was the average value of temperature data recorded by two K-type thermocouples placed within the fluidized-bed during the run.

The pyrolysis vapours, including aerosols, water and permanent gases produced from the thermal degradation of the organic fractions of the trommel fines, as well as fine solids (char and ash), were carried away from the reactor by the large flow of nitrogen. This is a main feature of fluidized bed reactor systems. On reaching the cyclone, most of the entrained solids were removed and transferred into the char pot. The vapours together with some solid residues fines that could not be removed by the cyclone, then passed through a liquid product collection system consisting of a water condenser, and a series of two dry ice/acetone condensers, where most of the condensable liquids were collected. However, some more volatile products could not be condensed and collected in the condensers and were trapped in the cotton wool filter. This could be attributed to the low partial pressure of the volatiles in the condensers due to the dilution effect of the large flow of nitrogen carrier gas. This problem is widely known in large-scale pyrolysis plants and can be solved by process optimization, which is a subject for further research. After the cotton wool filter, the nitrogen carrier gas together with the non-condensable pyrolysis gases passed through the gas meter where the volume of the exit gas was recorded. Each experiment was conducted three times and average yields reported.

2.3 Analyses of fast pyrolysis products

2.3.1 Liquid product

In total, there were six fractions of the liquid products based on the collection point within the pyrolysis rig. These include; (1) water-cooled condenser, (2) transition pipe 1, (3) dry ice acetone condenser 1, (4) transition pipe 2, (5) dry ice acetone condenser 2, and (6) cotton wool filter. For ease of handling all the liquid products obtained from fast pyrolysis process were then classified into primary condensates (water-cooled condenser product) and secondary condensate (the others). Both products consisted of mixtures of oil, water and fine solids.

Volumetric Karl-Fischer (KF) titration was used to determine the water content of all the fast pyrolysis primary and secondary condensate. The primary and secondary condensates were dissolved in a known volume of acetone (1 part of condensate to 6 parts of acetone) prior to analyses. Solids content in the primary condensate was determined using the vacuum filtration technique suggested by Oasmaa and Peacocke (2001). The primary condensate was filtered through a pre-dried and pre-weighed Whatman No. 2 qualitative filter paper with mean pore size of 8 µm. The product was then washed with excess amount of acetone until the filtrate was clear to ensure that there was no organic liquid left on the filter paper. The filter paper with the residue was air-dried for approximately 15 min and in an oven at 105 °C for around 2 h, cooled in a desiccator and weighed. Solvent-free primary and secondary condensates were analysed to determine their elemental (CHNS) analysis using CE-440 and Carlo Erba elemental analysers with ±0.3% absolute accuracy. Oxygen was obtained by difference.

2.3.2 Pyrolysis liquid product analysis by GC-MS

Compositional analysis of liquid product samples was performed using a PerkinElmer Clarus 680 GC-MS system. GC samples were prepared by mixing liquid product with GC grade acetone (1:6 vol/vol). 1 μL of the sample was filtered using a 0.2 μm pore size Sartorius filter, and was injected into the GC column via an injection port maintained at 300 °C, with 1:50 split ratio. The transfer line was held at 275 °C, while the detector temperature was at 250 °C. The GC oven programme was as follows: held constant at 50 °C for 2 mins, then ramped at 5 °C min^{-1} to 275 °C and held at 275 °C for 3 min. The programme lasted 50 min. Helium was used as the carrier gas with a constant flow of 15 ml min^{-1}. A column splitter was used to enable simultaneous detection of compounds separated on the columns by MS and FID detectors. Mass spectra were obtained using 70 eV ionisation energy in the molecular mass range of m/z = 35 - 300, with a scan time of 0.35 seconds. Assignments of the main peaks were made from mass spectral detection (NIST05 MS library).

2.3.3 Solid product analysis

Total solids from the fast pyrolysis was a combination of the solid residues collected in the char pot, reactor bed and metal transition pipe, and the solid fines or solids present in the liquid products. However, the char pot residue accounted for about 90 wt% of the total solids measured and was used for ash determination. The ash contents of char pot solid residues were determined according to the ASTM D1762-84 method (ASTM, 2013). In the procedure, between 4 and 5 g of solid residues was placed a pre-cleaned and pre-weighed crucible and heated in a furnace and heated to 750 °C for 6 h. After cooling in a desiccator for one hour, the crucible was weighed to the nearest 0.1 g. The ash content was obtained by difference and expressed as wt% of the solid residues with standard deviation from five replicate analyses. For each sample, the average of five samples was taken to reduce the deviation. CHNS analyses of the solid residues were also carried out using the same CE-440 and Carlo Erba elemental analysers.

2.3.4 Gas product analysis

During a pyrolysis run, the non-condensable gases were sampled every 3 min into a micro gas chromatograph with a thermal conductivity detector (TCD) from Varian Chromatography System Inc. (Kalgo, 2011; Banks, Nowakowski and Bridgwater, 2014). The gas components were separated on two columns; namely Varian CP-5A Molsieve held isothermally at 80 ºC (for H_2, CO, N_2 and O_2) and CP-PortaPLOT held isothermally at 90 ºC (for CO_2 and C_1-C_4 hydrocarbon gases prior to detection. Quantitation was achieved by external standard method by calibrating the detector response using a standard gas mix containing these gases at 3 vol% concentrations in nitrogen. The mass yields of the gas components (nitrogen-free) were calculated using the general gas equation, based on the gas volume composition obtained from GC analysis, total gas volume and the exit gas temperature and recorded pressure. The calorific values (as higher heating values, HHV) of gas product were estimated from the volume percentage of each gas component and their higher heating values, according to Eq.1.

$HHV\ (\mathrm{MJ}\ kg^{-1}) = \sum_{i=1}^{n}(x_i.HVV_i)$ ……………………………………………………Eq. 1.

Where;

i …n = each combustible component in the gas product

x = mass fraction of combustible components in gas product

HHV_i = higher heating value of each component in MJ kg^{-1}

2.3.5 Heating value of liquid and solid products

The standard bomb calorimeter method was used to determine the higher heating value for the primary condensate and solid products (ASTM, 2000). Results obtained from the bomb calorimeter experiment indicate the higher heating value (HHV) of the samples. In the procedure, approximately 1 g of solvent-free primary condensate was burnt completely at constant volume, in an excess oxygen environment in a steel vessel, called a bomb using a Parr 6100 calorimeter. Each experiment was repeated three times. The same procedure was repeated for the solid residues. In addition, the HHV of the solids were calculated using the generalised formula reported by Channiwala and Parikh (2002), according to equation 1;

$HHV = 0.3491C + 1.1783H + 0.1005S + 0.1034O – 0.0151N – 0.0211A$…………………….. (1)

Where; C = carbon wt%, H = hydrogen wt%, S = sulphur wt%, O = oxygen wt%, N = nitrogen wt% and A = wt% ash

2.4 Mass balance calculation

Mass balances (wt% on dry feed basis) were calculated based on mass of dry trommel fines processed and final fast pyrolysis products of liquid, solid residues and non-condensable gases. The solid residues were distributed into the bed material, char pot and liquid products. The bed material was weighed before and after reach experiment to determine the weight of solid residues that remained. The weight of ash in the char pot was determined after char burn-off, while ash contents in the liquid products was determined via filtration and weighing. All metal, glassware items and transition pipes used in the bench-scale pyrolysis unit were weighed before and after each run, to calculate the yields of pyrolysis products. The amount of trommel fines feedstock fed into the pyrolysis reactor was calculated from the difference between the weight of trommel fines added to hopper before and the trommel fines left in hopper after each experiment.

2.5 Fast pyrolysis energy recovery efficiency

To determine whether trommel fines samples can be used for energy recovery via fast pyrolysis, with significant reduction in mass and volume of the original waste, the fast pyrolysis energy recovery efficiency (η) was calculated based on the ratio of the energy content in the conversion products to that in the feedstock. In this case, the products of trommel fines fast pyrolysis conversion were the liquid and gas products as well as the char product obtained in the char pot. Therefore, energy recovery efficiency was obtained by using the higher heating values (HHV) and the mass of each component (m) as follows:

$$\eta\,(\%) = \frac{(\text{m HHV})\text{liquids}+(\text{m HHV})\text{ gas products}+(\text{mHHV})\text{solid products}}{(\text{m HHV})\text{feedstock}}\ \text{x}\ 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (2)$$

3 Results and Discussions

3.1 Effect of pyrolysis temperature on overall mass balance and product yields

Table 3 details an overview of the process parameters, product yields, product distributions and mass balance closure results obtained from the experiments. The resulting mass balances were compared to establish similarities between results. Reproducibility was more than 95%, so the highest mass balance closure obtained were reported and the rest are presented as standard deviations (Kalgo, 2011; Bank, Nowakowski and Bridgwater, 2014). As can be seen from Table 3, the mass balance closures were above 97% for TIR-400 and TIR-500, which showed acceptable accounting for the mass flows. However, the mass balance closure decreased with increasing temperature, with TIR-700 having the lowest mass balance closure. The relatively poor balances at higher temperatures was be largely due to the presence of unidentified gas components, formed from severe thermal degradation, whose peaks were observed in the GC outlines but not quantified.

Two sets of data for product gases have been included in Figure 2. One set of data represent the actual yields obtained from GC analysis, while the other set of data was obtained by difference after considering the yields of liquids and solids. Figure 2 therefore shows that there was a good agreement between two sets of data at the lower temperatures, with significant differences at higher temperatures. In fast pyrolysis, the liquid product is generally regarded as the main product, while solid products and permanent gases may be valuable by-products. Typically, liquid products contain some amount of water (Czernik and Bridgwater, 2004). This water is derived from the moisture in the feedstock and the water produced during fast pyrolysis reaction, which is called ‘‘reaction water”. In Table 3, only the reaction water is reported, and the non-aqueous part of bio-oil is then referred to as ‘‘organics”, which is the desirable product. This fraction is reported without the solids (ash-free). Results showed that pyrolysis temperatures have a dominant effect on the liquid product yield.

In general, the yields of total liquid increased with increasing pyrolysis temperature from 400 °C to 500 °C and then decreased at higher temperatures (Figure 2). The highest liquid yield was observed at TIR-500 (32.6 wt% dry basis) with a primary condensate organic yield of 12.5 wt% (daf) and secondary condensate organic yield of 7.00 wt% (daf). When compared to literature on pyrolysis of RDF, due to the similarity in composition with the trommel fines feedstock, the organic yield obtained here was smaller (Mohan et. al 2006; Chen et al., 2015; Ding et al., 2016). In addition, the reaction water yields were found to decrease with increasing temperature, indicating the possible consumption of the produced water in the chemical reactions occurring during fast pyrolysis at high temperatures (Chen et al., 2015; Ding et al., 2016).

The solid residues obtained from the fast pyrolysis of trommel fines ranged of 48 – 65 wt% on dry basis (Figure 2). This result was consistent with the high ash content (36.2 wt%, dry basis) of the feedstock. In general, it can be observed from Figure 2, that increasing temperature led to a slight decrease in solid residues, while gas yields increased. Hence, it was considered to use 700 °C as the maximum pyrolysis temperature, as higher temperatures would lead to more gasification. Such effect has been reported in previous studies, showing increased gas formation at the expense of liquid and solid products during high-temperature pyrolysis of different organic feedstock, using different reactor configurations (Luo et al., 2004; Lee et al., 2005; Tsai et al., 2007). The increase of gas yields with increasing temperature is possibly due to a combination of secondary thermal cracking of the evolved pyrolysis vapours and the catalytic effects of the ash via vapour-solid reactions at elevated temperatures (Lee et al., 2005; Pradhan, 2015; Renkonen, 2016). Some researchers have shown that the presence of certain types of ash (e.g. alkali metals and alkaline-earth metals) can promote the formation of solids, reaction water and gas products at the expense of pyrolysis liquid yield (Mohan et al., 2006; Buah et al., 2007; Zhou et al., 2013; Chen et al., 2014; Pradhan, 2015; Xue, Braden and Bai, 2017)

As seen in Table 3, the gaseous products contain mainly of carbon dioxide and propylene with small quantities of $C_1 – C_4$ hydrocarbon gases. Most of the gases identified, increased in their mass yields with increasing temperature. Moreover, it can be seen from Figure 3 that increasing pyrolysis temperature led to a decrease in CO_2 proportion in the gas product (Figure

3A) as other gases became prominent. This could be mainly because most of the CO_2 was already generated by carboxyl release at a relatively low temperature (Luo et al., 2004). In addition, the secondary thermal cracking of pyrolysis vapours produced CO and hydrocarbon gases rather than CO_2.

3.2 Effect of pyrolysis temperature on liquid product characteristics

The water content of the liquid products from pyrolysis has remained one of the factors affecting their quality and subsequent use. Certainly, the higher the reaction water yields, the higher the water content in the liquid products. The presence of water in the liquid products can be disadvantageous and advantageous. It reduces the heating value, especially the LHV and flame temperature and on the other hand, it improves the flow characteristics of pyrolysis liquid by reducing the viscosity (Czernik and Bridgwater, 2004).

The water contents of liquid products produced from trommel fines at different pyrolysis temperature are summarised in Table 4. It can be seen from Table 4 that operating temperatures has significant influence on the water contents of liquid products; they seemed to be higher at lower temperature especially in the secondary condensates, as more water condensed in the condensers operated at low temperatures. This agrees with a study by Lee et al., (2005), where fast pyrolysis of rice straw at different temperatures was investigated. The total water contents of trommel fines liquid products (primary and secondary condensate) were in the range of 50 – 78 wt%, which is higher than those of typical wood bio-oils and may need to be reduced prior to use. A promising route to lowering the amount of water in bio-oils has been proposed by Oasmaa et al. (2005), which involves the removal of water together with light reactive volatiles by increasing the condenser temperature to 50 ± 4 °C followed by the addition of alcohol (usually isopropanol) to improve the viscosity and stability of the bio-oils.

The solids contents entrained in the liquid products produced at different pyrolysis temperatures are also presented in Table 4. The solid content in the trommel fines liquid products increased with increasing temperature. They fluctuated in the range of 0 – 16.2 wt%, which was a higher range than those reported in literature (Miskolczi et al., 2013). Solids in bio-oils are usually composed of char fines entrained out of the cyclone and the secondary char formed by secondary reactions of pyrolysis vapours such as re-polymerization and condensation. In addition to these, the oils from trommel fines also contained inorganic materials (sand and glass fines) from the ash. The solids could escape the cyclone due to their very small particles (less than about 10 µm in diameter) and the high gas stream velocity in the cyclone. The main challenge was that once the solids got into the liquid products, it was difficult to remove by liquid filtration because of the highly viscous nature of the primary condensate.

Literature has shown that, by introducing a hot vapour filter prior to condensation units, the amounts of solids in liquid products can substantially be reduced (Chen et al., 2011; Pattiya and Suttibak, 2017). The solids present in in the liquid product can cause erosion and blockages to equipment such as nozzles, valves and pumps, (Czernik and Bridgwater, 2004). Additionally, the inorganic compounds present in the solids are important to bio-oils ageing characteristics as they appear to catalyse polymerisation reactions during storage, leading to increased viscosity and growth in the apparent diameter of the suspended char (Diebold, 2000). Accordingly, liquids with lower solids content are generally preferred. However, the solids content of liquid product may not be an important issue, if the product is a mixture of bio-oil and solid char in the form of slurry. This slurry which can contains up to 90% of energy from the feedstock could be used as a feedstock for gasification process to produce syngas or producer gas. In fact, the slurry is commercially known as Bio-Oil Plus™ from Dynamotive Energy Systems Corporation, which can be used as fuel in boilers.

The elemental compositions of both the primary and secondary condensate liquids are also listed in Table 4. The percentages of carbon for both primary and secondary condensate increased with increasing temperature until reaching a maximum. With regards to nitrogen contents, increase in temperature led to an increase in nitrogen content for both the primary and secondary condensates and are higher than typical wood bio-oil, which resulted from the high nitrogen content in the trommel fines feedstock. The presence of textile materials such as those made from polyamides may have significantly increased the nitrogen contents of the trommel fines; which upon thermal degradation would form nitrogen-containing volatile compounds, which condensed into liquids after cooling in the condensers.

Moreover, there was more nitrogen in the secondary condensates than in the primary condensates, possibly due to the high volatility of the nitrogen-containing degradation products, which were trapped in the colder condenser. The presence of nitrogen compounds can be a drawback when burning the liquids because of the high potential for NOx emissions. This problem may be prevented by pre-treatment such as the washing of the feedstock with distilled water prior to pyrolysis (Lee et al., 2005). The pre-treatment has shown to also remove some alkali metals such as sodium and potassium that are known to have adverse catalytic effect during fast pyrolysis reactions (Lee et al., 2005).

The heating values of the primary and secondary condensate liquids are also shown in Table 4. It was found that the heating values increased with increasing temperature until reaching a maximum then further increase led to slight decrease for both the primary and secondary condensate with TIR-500 liquids having the highest values for both the primary and secondary condensate 32 MJ kg^{-1} and 17.45 MJ kg $^{-1}$ (dry basis) respectively. The HHV of the primary condensate was found to be higher when compared to literature on pyrolysis of biomass (Diebold, 2000; Czernik and Bridgwater, 2004; Lee et al. 2005) and has potential for energy recovery. The fractional plastic content of the trommel fines feedstock may be responsible to the high heating value.

3.3 Effect of pyrolysis temperature on composition of organic liquid products

The organic liquid products produced from pyrolysis temperature investigation are composed of different classes of organic compounds, which are derived primarily from the de-polymerization and fragmentation reactions of the organic components of the original feedstock, namely the biogenic and plastic fractions in the trommel fines (Mohan et al., 2006). The chromatograms of the primary and secondary condensate liquids from TIR-500 experimental run are shown in Figure 4, indicating the different profiles of compounds present in both fractions. These chromatograms show that majority of the compounds in the primary condensate had longer retention times in the GC columns compared to compounds in the secondary condensates. Therefore, the secondary condensates contained lighter, more volatile organic compounds that the primary condensates as shown later in Figure 5.

The major organic compounds have been classified into groups including, oxygenates, carboxylic acids, amines, phenols, aromatic hydrocarbons and others. Oxygenates included compounds such as ketones and aldehydes e.g. cyclopentanones, cyclopentenones, furfural and their alkylated derivatives, from pyrolysis of the sugar fractions (cellulose and hemicellulose) of biomass. Aromatic hydrocarbons included styrene, azulene, naphthalene and bibenzyls; these compounds have been reported as products of polystyrene pyrolysis (Muhammad, Onwudili and Williams, 2015). Phenols included phenol, alkyl phenols and methoxyphenols such as methylphenols and dimethylphenols, which are common compounds from lignin pyrolysis (Zhou et al., 2015). Several amines N-containing compounds were detected in the liquid products including 1-propenamine, pyridine and methyl pyridine, which could be from the pyrolysis of textile materials made from polyamides.

Figure 5 presents the relative compositions, in terms of peak area percent, of the primary and secondary condensates in relation to pyrolysis temperatures. The compounds with the largest peak areas, up to about 60% of compounds in each sample, were selected for detailed evaluation. The primary condensates consisted of heavier compounds including phenols and 2-ringed aromatic hydrocarbons, while the secondary condensates contained a number of lighter compounds such as the ketones and aldehydes (oxygenates), amines and lighter aromatic hydrocarbons (e.g. propynyl benzene and azulene). Increase in temperature increased the presence of phenolic and aromatic hydrocarbon compounds in the primary condensate (and Figure 5A). The increased formation of these compounds is known to be promoted during high temperature pyrolysis of biomass through secondary reactions such as radical combinations and cyclization (Diels-Alder reaction), aromatisation, deoxygenation, demethoxylation and demethylation (Ashmadi et al., 2011; Ledesma et al., 2013; Zhou et al., 2015).

On the contrary, in the secondary condensate (Figure 5B), the peak area percent of lighter compounds decreased with increasing temperature. These trends agree with trends seen in literature as increase in temperature would have let to more cracking and increases in gas yields as seen on Table 3. The secondary condensate liquid fraction collected from the dry ice condensers showed the presence of nitrogen-containing organic compounds (Figure 5B). These compounds were in the form of amines, pyridines and their derivatives. This finding is in line with the result of the elemental analysis of the secondary condensate liquid which shows an increase in nitrogen content with increasing temperature (Table 4).

3.4 Effect of pyrolysis temperature on solid residues characteristics

The solid residues obtained from this work, expectedly contained a mixture of ash (inorganic material) and char. Ash content, elemental composition, and calorific value of the solid products obtained from fast pyrolysis of trommel fines are tabulated in Table 5. The degradation of the organic fraction of the feedstock via fast pyrolysis process would leave the ash in the solid product (Silva et al., 2015; Rotheut and Quicker, 2017; Zaini et al., 2019). The ash content in the solid residues ranged from 62 - 87 wt% (dry basis), with TIR-500 having the highest ash content of 86.3 wt%. Increase in temperature above 500 °C lead to a slight decrease in the ash content (Table 5) and this is possibly due to the secondary decomposition of solid residues (such as carbonates) at elevated temperatures (Scott et al., 1988), which lead to an increase in gas yield (Figure 2). At lower temperatures, there was more char in the solid residues (Table 5).

The elemental compositions and heating value of solid products are also listed in Table 5. The percentage of carbon did not show a clear trend but mirrored the proportion of char in the solid residues at different pyrolysis temperatures. The heating values of the solid products corresponded to the carbon contents. The HHV were in the range of 4 - 8 MJ kg $^{-1}$ dry basis, giving a maximum value at the lower temperature. The low calorific value of the solid product would not make it a viable source of process heat but could be combusted in cement kilns and the ash incorporated in building materials (if non-hazardous).

A scan of the ash in the feedstock was carried out using a Bruker S8 Tiger X-ray Fluorescence (XRF) spectrometer, capable of quantifying elements from sodium to uranium. The major elements in the component with concentrations > 0.1 wt% included calcium, silicon, lead, chlorine, iron, potassium, aluminium, copper, sulphur, manganese, niobium, phosphorus, zinc, magnesium and titanium (Onwudili and Eke, 2019). Hence apart from chlorine, these elements (mainly as their oxides) would remain in the solid residues, which may be burnt off at cement kilns, milled and in combination with clay, lime and cement mortar can be used as an additive for plaster or for bricks and concrete elements at a ratio of up to 80%. Such blending has been reported to create inside walls with excellent insulation and breathing properties, able to maintain humidity levels in a room at 45 – 70% (Schmidt, 2014).

Alternatively, the solid residues may be used in suitable biochar applications such as in soil amendments as fertilizer and for carbon sequestration. When used as a soil amendment, biochar has been reported to boost soil fertility and improve soil quality by raising soil pH, increasing moisture holding capacity, attracting more beneficial fungi and microbes, improving cation exchange capacity (CEC), and retaining nutrients in soil (Lehmann, Gaunt and Rondon, 2006; Lehmann, 2007; Winsley, 2007; Gaunt and Lehmann, 2007; Laird, 2008). Biochar may persist in soil for millennia because it is very resistant to microbial decomposition and mineralisation.

3.5 Energy recovery from pre-treated trommel fines

Figure 6 shows the effect of temperature on the fast pyrolysis process conversion efficiency of dry physically pre-treated trommel fines samples calculated using the calorific values of the liquid, solid (char pot) and gas products. The char content left in the bed material was not considered as it would not be readily available for immediate use. Therefore, Figure 6 reflect the energy yields based on the liquid, char pot residues and gas products from the fast pyrolysis of trommel fines. The energy recovery efficiency ranged between 63 – 70%, generally increasing with increasing pyrolysis temperature from 400 °C to 700 °C, except for a dip at 600 °C. Figure 6 shows that the liquid product accounted for over 56% of the recovered energy from the trommel fines feedstock at 500 °C. Whereas, at higher temperatures, the contributions of gas products to the recovered energy became more dominant, such that at 700 °C, the gas products contributed 50% to the energy yields.

From these results, it is clear that running the fast pyrolysis tests at temperatures around 500 °C, gave the highest liquid products. Literature shows that at around 500 °C, fast pyrolysis is used to obtain the highest liquid yields from various organic feedstocks including biomass and plastics. Therefore, trommel fines may be co-processed with other feedstock without major changes to fast pyrolysis process conditions. Indeed, co-processing of trommel fines with biomass would reduce the operational impact of its high ash content and possibly give a liquid product with better quality, especially in terms of calorific values.

4. Conclusion

Energy recovery from a physically pre-treated trommel fines feedstock has been investigated in a bubbling fluidised bed reactor in relation to pyrolysis temperature. The optimum reaction temperature to obtain the highest pyrolysis liquid was 500 °C (33 wt % dry basis). It was found that trommel fines produced less pyrolysis liquids (approximately 13 - 33 wt%, dry basis) compared to woody biomass (50 - 75 wt%), mainly due to the high ash content (36 wt%) of the former. Similar to other pyrolysis studies, reaction temperature had a dominant effect on the fast pyrolysis product yields. However, the dramatic increase in gas yields above 500 ºC, could attributed to synergistic catalytic cracking effect of the high ash content. The trend in the yields of pyrolysis products mirrored the calculated energy recovery efficiency profile; showing that non-volatilised solids, liquid products and gas products dominated the recovered energy at 400 °C, 500 °C and 700 °C, respectively. The high ash content of the feedstock (36 wt %, dry basis) resulted in a large proportion of solid residues in the char pot, which was found to contain mostly non-hazardous earth materials and could be used by the construction industry. Subsequent accumulation of large quantities of solid residues in the char pot may cause safety and operability problems during long periods of rig operation. Possible solutions would involve redesigning the ring to allow for intermittent/periodic removal of accumulated solids and/or the use of a char pot with larger volume. Overall, the results of this work showed that the BFB fast pyrolysis reactor could handle the high ash content after size reduction of the trommel fines feedstock, while producing liquid and gas products as valuable recovered energy carriers.

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References

Asmadi, M.; Kawamoto, H.; Saka, S., 2011. Gas- and solid/liquid-phase reactions during pyrolysis of softwood and hardwood lignins. J. Anal. Appl. Pyrolysis, 92, 417−425.

ASTM, 2000. ASTM D2015 Standard Test Method for Gross Calorific Value of Coal and Coke by the Adiabatic Bomb Calorimeter. American Society for Testing and Materials International, United States

ASTM D1762 – 84, 2013. Standard Test Method for Chemical Analysis of Wood Charcoal. American Society for Testing and Materials International, United States

Ates, F., Miskolczi, N., Borsodi, N., 2013. Comparison of real waste (MSW and MPW) pyrolysis in batch reactor over different catalysts. Part I: product yields, gas and pyrolysis oil properties. Biores. Technol. 133, 443–454.

Banks, S. W., Nowakowski, D.J., Bridgwater, A.V., 2014. Fast pyrolysis processing of surfactant washed Miscanthus. Fuel Proc. Technol. 128, 94-103.

Bosmans, A., Vanderreydt, I., Geysen, D., Helsen, L., 2013. The crucial role of waste-to-energy technologies in enhanced landfill mining: a technology review. J. Cleaner Prod. 55, 10-23.

Channiwala, S.A., Parikh, J., 2002. A unified correlation for estimating HHV of solid, liquid and gaseous fuels. Fuel 81, 1051-1063.

Chen, S., Meng, A., Long, Y., Zhou, H., Li, Q. and Zhang, Y., 2015. TGA pyrolysis and gasification of combustible municipal solid waste. J. Energy Institute 88(3), 332-343.

Chen, T., Wu, C., Liu, R., Fei, W. and Liu, S., 2011. Effect of hot vapour filtration on the characterization of bio-oil from rice husks with fast pyrolysis in a fluidized-bed reactor. Biores. Technol. 102(10), 6178-6185.

Czernik, S., Bridgwater, A.V., 2004. Overview of applications of biomass fast pyrolysis oil. Energy Fuels 18, 590–598.

Diebold, J.P., 2000. A Review of the Chemical and Physical Mechanisms of the Storage Stability of Fast Pyrolysis Bio-Oils. National Renewable Energy Laboratory (NREL). NREL/SR-570-27613.

Ding, K., Zhong, Z., Zhong, D., Zhang, B., Qian, X., 2016. Pyrolysis of municipal solid waste in a fluidized bed for producing valuable pyrolytic oils, Clean Technol. Environ. Policy 18, 1111-1121.

Eke, J., Onwudili, J. A. and Bridgwater, A.V., 2017. Physical Pretreatment of biogenic-rich trommel fines for fast pyrolysis. Waste Management. 70, 81-90.

Fitzgerald, G.C., 2013. Pre-processing and treatment of municipal solid waste (MSW) prior to incineration. In. Klinghoffer, N.B. and Castaldi, M.J. (eds). Waste to Energy Conversion Technology, 55-71. Woodhead Publishing Limited, Cambridge

Gaunt, J., Lehmann, J., 2008. Energy balance and emissions associated with biochar sequestration and pyrolysis bioenergy production. Environ. Sci. Technol. 42, 4152- 4158.

Grammelis, P., Basinas, P., Malliopoulou, A., Sakellaropoulos, G., 2009. Pyrolysis kinetics and combustion characteristics of waste recovered fuels. Fuel 88, 195-205.

Grieco, E.M., Baldi, G., 2012. Pyrolysis of polyethylene mixed with paper and wood: interaction effects on tar, char and gas yields, Waste Management 32, 833– 839.

HMRC, 2014. Landfill Tax: Liability of waste ‘fines’. Her Majesty Revenue & Customs. Webpage:Online:https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/325100/Landfill_tax_condoc.pdf. [Accessed 21 May 2019].

Kalgo, A. S., 2011. The Development and Optimisation of a Fast Pyrolysis Process for Bio-oil Production, Aston University, PhD Thesis.

Laird, D. A., 2008. The charcoal vision: A win-win-win scenario for simultaneously producing bioenergy, permanently sequestering carbon, while improving soil and water quality. Agron. J. 100, 178-181.

Ledesma, E.B., Campos, C., Cranmer, D.J., Foytik, B.L., Ton, M.N., Dixon, E.A., Chirino, C., Batamo, S., Roy, P., 2013. Vapor-phase cracking of eugenol: distribution of tar products as function of temperature and residence time. Energy and Fuels 27: 868–878

Lee, K.H., Kang, B.S., Park, Y.K., Kim, J.S., 2005. Influence of reaction temperature, pre-treatment, and a char removal system on the production of bio-oil from rice straw by fast pyrolysis, using a fluidized bed. Energy Fuels 19, 2179-2184.

Lehmann, J., 2007. Bio-energy in the black. Front. Ecol. Environ. 5, 381-387.

Lehmann, J., Gaunt, J., Rondon, M., 2006. Bio-char sequestration in terrestrial ecosystems: a review. Mit. Adapt. Strat. Global Chang 11, 403-427.

Luo, Z., Wang, S., Liao, Y., Zhou, J., Gu, Y., Cen, K., 2004. Research on biomass fast pyrolysis for liquid fuel. Biomass and Bioenergy 26, 455-462.

Malkow, T., 2004. Novel and innovative pyrolysis and gasification technologies for energy efficient and environmentally sound MSW disposal. Waste Management. 24, 53-79.

McKendry P., 2002. Energy production from biomass (Part 2): conversion technologies. Biores. Technol. 8, 37-54

Miskolczi, N., Ates, F., Borsodi, N., 2013. Comparison of real waste (MSW and MPW) pyrolysis in batch reactor over different catalysts. Part II: contaminants, char and pyrolysis oil properties. Biores. Technol. 144, 370-379.

Mohan, D., Pittman, C.U., Steele, P.H., 2006. Pyrolysis of wood/biomass for bio-oil: a critical review. Energy and Fuels 20, 848-889.

Muhammad, C., Onwudili, J.A., Williams, P.T., 2015. Thermal degradation of real-world waste plastics and simulated mixed plastics in a two-stage pyrolysis-catalysis reactor for fuel production. Energy and Fuels 29, 2601-2609,

Oasmaa, A., Peacocke, C., 2001. A guide to physical property characterisation of biomass-derived fast pyrolysis liquids. Technical Research Centre of Finland, Espoo.

Oasmaa, A., Sipila, K., Solantausta, Y., Kuoppala, E., 2005. Quality improvement of pyrolysis liquid: effect of light volatiles on the stability of pyrolysis liquids. Energy and Fuels 19, 2556-2561.

Onwudili, J. A. and Eke, J., 2019. Effects of ash removal by agitated aqueous washing and sedimentation on the physico-chemical characteristics and fast pyrolysis of trommel fines. J. Energy Institute 93(1), 312 – 323.

Pattiya, A. and Suttibak, S. (2017). Fast pyrolysis of sugarcane residues in a fluidised bed reactor with a hot vapour filter. J. Energy Institute 90(1), 110-119.

Pitchell, J., 2014. Municipal solid waste processing: material recovery facilities. Waste Management Practices: Municipal, Hazardous and Industrial. 2nd Edition, 165-196. CRC Press, London.

Pradhan, U., 2015. Physical treatments for reducing biomass ash and effect of ash content on pyrolysis products. MSc Dissertation, Auburn University, Alabama, USA. Available online: https://etd.auburn.edu/bitstream/handle/10415/4726/Master%20thesis_Ujjain.pdf?sequence=2&isAllowed=y . [Accessed May 1, 2019].

Renkonen, S., 2016. Removal of alkali metals for the enhancement of fast pyrolysis process. Master's Thesis. Aalto University, Espoo, Finland. Available online: https://cris.vtt.fi/en/publications/removal-of-alkali-metals-for-the-enhancement-of-fast-pyrolysis-pr. [Accessed: May 16, 2019].

Rotheut, M., Quicker, P., 2017. Energetic utilisation of refuse derived fuels from landfill mining. Waste Management, 62, 101–117

Schaefer, W.D., 1975. Disposing of solid wastes by pyrolysis. Environ. Sci. Technol. 9, 98-98.

Schmidt, H. P., 2014. The use of biochar as building material, Biochar Journal, Arbaz, Switzerland. ISSN 2297-1114 www.biochar-journal.org/en/ct/3. Accessed: 04.03.2019

Scott, D.S., Piskorz, J., Bergougnou, M.A., Graham, R., Overend, R.P., 1988. The role of temperature in the fast pyrolysis of cellulose and wood. Ind. Eng. Chem. Res. 27, 8-15.

Silva, R.B., Martins-Dias, S., Arnal, C., Alzueta, M.U., Costa, M., 2015. Pyrolysis and char characterization of refuse-derived fuel components. Energy and Fuels, 29,1997–2005.

Sørum, L., Gronli, M.G., Hustad, J.E., 2001. Pyrolysis characteristics and kinetics of municipal solid wastes. Fuel 80, 1217-1227.

Tsai, W.T., Lee, M.K., Chang, Y.M., 2007. Fast pyrolysis of rice husk: product yields and compositions. Biores. Technol. 98, 22-28

Winsley, P., 2007. Biochar and bioenergy production for climate change mitigation. New Zealand Sci. Review 64, 5-10.

Zaini, I. N., López, C.G., Pretz, T., Yang, W., Jönsson, P.G., 2019. Characterization of pyrolysis products of high-ash excavated-waste and its char gasification reactivity and kinetics under a steam atmosphere. Waste Management, 97, 149-163.

Zhao, L., Chen, D.Z., Wang, Z.H., Ma, X.B., Zhou, G., 2011. Pyrolysis of waste plastics and whole combustible components separated from municipal solid wastes: Comparison of products and emissions. In: Proceedings of the Thirteen International Waste Management and Landfill Symposium, 3–6 October 2011, Sardinia, Italy.

Zhou, H., Wu, C., Onwudili, J.A., Meng, A., Zhang, Y., Williams, P.T, 2015. Polycyclic aromatic hydrocarbons (PAH) formation from the pyrolysis of different municipal solid waste fractions. Waste Management 36, 136-146.