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Products from the high temperature pyrolysis of RDF at slow and rapid heating rates

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Abstract

The high-temperature pyrolysis behaviour of a sample of refuse derived fuel (RDF) as a model of municipal solid waste (MSW) was investigated in a horizontal tubular reactor between 700 – 900 °C , at varying heating rates, and at an extended vapour residence time. Experiments were designed to evaluate the influence of process conditions on gas yields as well as gas and oil compositions. Pyrolysis of RDF at 800 °C and at rapid heating rate resulted in the gas yield with the highest CV of 24.8 MJ m^{-3} while pyrolysis to 900 °C at the rapid heating rate generated the highest gas yield but with a lower CV of 21.3 MJ m^{-3}. A comparison of the effect of heating rates on oil products revealed that the oil from slow pyrolysis, contained higher yields of more oxygenates, alkanes (C8 to C39) and alkenes (C8 to C20), while the oil from rapid pyrolysis contained more aromatics, possibly due to the promotion of Diels-Alder-type reactions.

1.0   Introduction

There is a continuously growing need for new and sustainable sources of energy in the world as our populations grow and countries become more developed. There is also an increased demand for renewable sources of energy, resulting in increased interests in the processing of municipal solid waste (MSW) as an energy resource both by biochemical and thermochemical means. Among the thermochemical technologies for MSW conversion,

pyrolysis is arguably, the most versatile in relation to the flexibility of obtaining primary products. The application of pyrolysis technology to MSW is quite promising as the energy content of the MSW can be extracted in the form of primary pyrolysis products including gas, liquid and solid product [1]. The production of the product fraction of choice (gas, liquid or solids) from RDF pyrolysis can be maximised by controlling the basic process conditions of temperature, heating rate, residence time etc. These primary products can be used directly for energy or subsequently converted into other fuels and or feedstock. However there are problems with the pyrolysis of MSW, especially due to its heterogeneity [2], which makes for inconsistent energy characteristics and lack of uniform thermal behaviour . One method of overcoming this problem involves converting MSW into refuse derived fuel (RDF). This process involves the densification of the combustible fractions of MSW, usually into pellets, after other non-combustible fractions like metals and glass have been recycled. This creates a feedstock with a; more uniform composition, relatively constant density and size, easier transport logistics and higher heating value than raw MSW. RDF is therefore a better feedstock for thermal conversion, including via pyrolysis, than MSW [3].

Literature shows that pyrolysis of biomass and MSW is usually carried out at temperatures between 400 °C and 600 °C [4-8]. The yields of the three product phases (gas, liquid and solid) can be largely controlled by the heating rates applied within this temperature range. During fast heating rates oil is the dominant product, while slow heating rates give a dominant solid product. In addition, the gas fractions tend to increase with increased pyrolysis temperatures. Velghe et al. [4] studied the slow and fast pyrolysis of MSW at temperatures up to 550 °C and reported maximum solids yield at slow pyrolysis to 550 °C while maximum oil yield was reported for fast pyrolysis to 510 °C. Results showed that higher temperatures favoured gas yields. Miskolczi et al. [5] conducted the pyrolysis of RDF in a two stage reactor at temperatures of 550 °C and 450 °C for the first and second stage

(catalytic) respectively and reported oil, gas and char yields of 67.3, 10.2 and 18.4 wt% for the first stage temperature of 550 °C.

Pyrolysis oils from MSW are often a mixture of several organic compounds with different functional groups, making its direct application difficult without further processing. For this reason, conversion of MSW to gas represents a refining process in which the lightest possible molecules are obtained. This is the objective of conventional gasification which converts biomass and MSW to mainly hydrogen and carbon monoxide. However, the production of a gas product with high content of hydrocarbon gases, rather than hydrogen may sometimes be expedient from the utilization point of view. There are still problems with hydrogen storage, whereas technologies for the storage and utilization of hydrocarbon gases have matured. Hence, the essence of high-temperature pyrolysis would be to obtain high yields of gas products, with high calorific values.

There are however few works available on the production of gases from fast pyrolysis of MSW at much higher temperatures. High-temperature pyrolysis produces a high yield of gas along with tarry oil and solid products. Garcia et al [9] investigated the pyrolysis of MSW at temperatures between 700 and 850 °C, and reported that gas yield increased from 41.1 to 56 wt%. This paper investigates high-temperature pyrolysis of RDF at different heating rates between 700 and 900 °C in a horizontal tubular reactor. The objective is to determine if there are any relationships between the yields of products, the characteristics of the RDF sample including its composition, and the pyrolysis conditions including heating rate.

2.0   Materials and Methods

2.1   Materials.

In this present study refuse derived fuel (RDF) pellets of approximately 16 mm diameter and 80 mm length were obtained from a UK MSW treatment facility. In order to increase the

sample homogeneity, the RDF pellets were thoroughly mixed, ground and then sieved to obtain 1mm particle size used in this study

2.2 Characterisation of feed sample

The moisture, volatile, fixed carbon and ash content of the fresh RDF were determined by proximate analysis using a Stanton-Redcroft Thermogravimetric analyser (TGA). Moisture content was determined according to EN 15414-3, volatile content was determined according to EN 15402, ash content was determined according EN 15403, while fixed carbon was determined as the difference of moisture, volatile and ash contents from 100%. The TGA temperature programme was set to heat the sample from 25 °C to 110 °C at a heating rate of 25 °C/min and a hold time of 10 min in nitrogen, then to 900 °C at 25 °C min^{-1} for 20 min in nitrogen and finally to 910 °C at 10 °C min^{-1} for 20 min in air. The TGA programme was capable of indicating separate maxima for the degradation temperatures of biogenic and plastic fractions of RDF, respectively. Elemental analysis to determine the carbon, hydrogen, nitrogen and sulphur contents of RDF were carried out with a Carlo Erba Flash EA 1112 elemental analyser, while the oxygen content was determined by difference. Table 1 shows the results of the proximate analysis and the elemental analysis of the 1mm samples of RDF. The table also shows the characteristics of separate samples of cellulose and a mixed waste plastic samples for comparison.

2.3 Pyrolysis Reactor

Pyrolysis experiments were carried out in a horizontal tubular reactor, shown in Fig. 1, which was designed for this purpose. The reactor was made up of a horizontal stainless steel cylindrical tube of length 650 mm and internal diameter of 11 mm. The reactor was heated externally by an electrical tube furnace which provided a heated zone of length 450 mm and could be easily controlled to provide the desired final temperature and heating. The sample

was introduced to the reactor via a sample boat, which was a cylindrical tube with a cup at its end for holding the sample. The sample boat was designed to be easily, horizontally inserted into and withdrawn from one end of the reactor, placing the cup at the centre of the reactor's heated zone for effective heating. A thermocouple was also integrated into the sample boat, designed to be placed concentric to the walls of the sample boat, thereby providing the temperature at the centre of the sample. Tests were carried out in order to investigate the effects of temperature (700, 800 and 900 °C) and heating rates at the sample centre on the pyrolysis of the RDF. Experiments were performed with 1 g of the RDF loaded unto the sample boat and inserted into the reactor which was continually purged with nitrogen at a flow rate of 100 ml/min. The volatiles residence time within the reactor was estimated as 9 sec. The reactor was heated to the desired final temperatures and at the desired furnace heating rates of (5, 20, 90 and 350 °C min^{-1}), these were found to be very close to the heating rate for the sample as measured by the thermocouple. The heating rate was determined by the equation.1.

$$dT/dt = (T_2 - T_1) / (t_2 - t_1) \ldots\ldots\ldots\ldots(1)$$

Where, T_2 is the final pyrolysis temperature

T_1 is the initial sample temperature

$t_2 - t_1$ is the time taken from the start of the experiment till the RDF attains final temperature.

.Pyrolysis volatile products were purged from the reactor by the nitrogen flow into two sets of glass condensers, one was immersed in water and the other with a glass wool trap was immersed in dry ice in order to trap the liquid products. The non-condensable gases were finally collected in a sampling bag for off-line analysis by gas chromatography. Solid products remained in the sample boat and were weighed and collected for analysis after the reactor cooled. Each experiment was carried out twice in order to determine the repeatability

of each experiment and the reliability of the pyrolysis reactor, under identical conditions. Standard deviations on product yields were within 5%.

2.4   Method development for tar/oil sampling and analysis

The tar/oil products trapped in the condensers for each experiment were weighed and then collected for analysis by gas chromatography/mass spectrometry (GC/MS). The two condensers collected the tarry products which were brownish in colour for the first condenser, while the product in the second condenser was a mixture of water and a pale yellow liquid. During sampling, the tar products in the condensers were separated into two fractions namely; the hexane-soluble fraction and the dichloromethane-soluble fraction. In the procedure, the condensers were initially rinsed with minimal aliquots of hexane in order to collect the hydrocarbons into the hexane fraction. After this, minimal volume of dichloromethane was used to dissolve and collect the remaining tars. This enabled the separate analysis of these fractions with minimal co-elutions and mis-identification of the compounds.

Before analysis in the GC/MS/MS, each fraction of tar/oil product was passed through a packed column of anhydrous sodium sulphate to remove water. This was followed by a further cleaning procedure in which the fractions were passed through packed EPH columns containing a sorbent of mixed silica and alumina, designed to fractionate aliphatic and aromatics from petroleum hydrocarbons. In this procedure, one EPH column was used for the clean-up and fractionation of the oil and tar products from each experiment. The hexane fraction was first passed through the EPH column and eluted with hexane to obtain the aliphatic hydrocarbons fraction. Then the DCM fraction was also passed through the same column and eluted with more dichloromethane solvent to obtain the aromatic hydrocarbon/oxygenates fraction. The EPH columns were supplied by Biotage, a Swedish company.

Appropriate dilutions of the prepared fractions were made prior to GC/MS/MS analysis. Identification and quantification was carried out using external standard method. For the aliphatic compounds a calibration curve was developed using a standard mixture of $C_8 - C_{40}$ compounds obtained from Sigma-Aldrich UK. In addition, standard solution of 36 aromatic compounds was prepared and used to create 4-point calibration curves for their analysis. The GC/MS/MS system consisted of a Varian 3800-GC coupled to a Varian Saturn 2200 ion trap MS/MS equipment. The column used was a 30m x 0.25mm inner diameter Varian VF-5ms (DB-5 equivalent), while the carrier gas was helium, at a constant flow rate of 1 ml min^{-1}. The GC injector was held at 290 °C. The oven temperature programme was as follows; 40 °C, held for 2 min and ramped to 280 °C at a rate of 5 °C min^{-1} and then held at 280 °C for 10 min., the transfer line temperature was 280 °C, manifold was at 120 °C and the trap temperature was held at 200 °C. Spectral searches on the installed NIST2008 library were used to qualitatively identify the major 'unknown' compounds in the oil products.

2.5   Gas Analysis

Non-condensables were collected in the sample gas bag and analysed by GC. A Varian 3380GC with dual packed columns and dual thermal conductivity detectors (GC/TCD) was used to analyse and determine the permanent gases (H_2, CO, O_2, N_2 and CO_2). The column for CO_2 analysis was of 2 m length by 2 mm diameter with Haysep $80 - 100$ mesh packing material. Analysis for H_2, CO, O_2 and N_2 was carried out in a second column of 2m length by 2 mm diameter packed with $60 - 80$ mesh molecular sieve. The GC oven was held at 40 °C during the analysis while the detector oven and filament temperatures were at 120 °C and 160 °C respectively. The carrier gas was Argon. A second Varian 3380 GC with a flame ionization detector (GC/FID) was used to analyse and determine the $C_1 - C_4$ hydrocarbons (CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_8 and C_4H_{10}) in Nitrogen carrier gas. The column was 2 m length by 2mm diameter, packed with Haysep $80 - 100$ mesh. The GC oven temperature

was set to 60 °C for 3 min and ramped to 100 °C at 5 °C min^{-1} held for 3 min and finally heated to 120 °C at 20 °C min^{-1} held for 17 min. The gross calorific value (GCV) of the gases where calculated from the equation 2 below

$$GCV = CV_m / Z_m \ldots\ldots\ldots\ldots\ldots\ldots\ldots..(2)$$

Where CV_m is product of the mole fractions and the calorific values of the individual gases

Z_m is the compressibility factor of the gases.

2.6   Solids analysis

The carbon deposits on the reactor wall together with the residue left over on the sample boat after pyrolysis were weighed and collected as the reacted solid residue. The surface area of reacted RDF solids were measured using the Brunauer, Emmett and Teller (BET) method via nitrogen adsorption in a Quantachrome Corporation (FL, US) Autosorb 1-C instrument. The gross calorific value (GCV) of the produced solids was determined using a bomb calorimeter.

3.0   Results and Discussion

3.1.1   RDF characteristics

The elemental analysis results earlier presented in Table 1 indicate that the RDF sample has similar hydrogen and carbon contents to the cellulose sample. These in addition to the high oxygen content suggested that the RDF contained much more biogenic fraction than plastics. Such high oxygen content is typical of RDF in literature [10, 11], mostly as a result of the chemically bound oxygen in the cellulosic fractions of the paper, cardboard and wood that make up RDF. The high ash and fixed carbon contents of the RDF was mostly responsible for the lower contents of volatile matter compared to the cellulose and plastic samples. The presence of silica and other inorganic materials often contribute to high ash contents of RDF,

while other easily carbonized organic materials other than common plastics and cellulose would be responsible for the much higher fixed carbon contents. The thermal degradation behaviours of the RDF, cellulose, mixed waste and simulated RDF samples are depicted in Fig 2, which shows the rate of weight loss and the derivative (dTG) curve and temperature with reference to time. TGA experiments were carried out with a sample mass of 10 mg using a heating rate of 10 °C min^{-1}. The dTG in Fig. 2a shows four major peaks for RDF. The first and the last peaks from the left side of Fig. 2a represent weight losses due to moisture release and the combustion of the fixed carbon, at the 100 °C region and at the introduction of air at the 910 °C temperature regions, respectively. The two centre peaks which are made up of a major peak between 200 and 425 °C, and a minor peak from 425 to 565 °C, represent the decomposition of the volatiles in RDF. However it is important to note that the volatile decomposition of RDF continued gradually up till 800 °C, which may be due to the presence of lignin [12, 13] in the biogenic fraction of the RDF. The TGA/DTG profile of the RDF mirrored those of a combination of the cellulose (major biomass component) and mixed waste plastics. The degradation of cellulose (Fig. 2b) coincided with peak 2 of Fig. 2a, while the degradation of the waste plastics (Fig. 2c) also coincided with peak 3 in the TGA/DTG of the RDF sample. This observation provided further confirmation that the 2 volatile decomposition peaks from the RDF TGA pyrolysis were mostly from the degradation of cellulosic matter and plastics.

The degradation of cellulosic matter has been reported to take place around the temperature ranges of 200 to 400 °C [11, 14] while plastic decomposition was reported to occur around the ranges 425 to 565 °C [10, 15]. The mass loss analysis of the TGA results showed that the RDF sample was roughly composed of 13 wt% ash and 83 wt% fuel (organic) material. In addition, the DTG analysis indicated that the fuel fraction consisted of 79% biogenic material and 21% plastic fractions. To confirm this observation, a simulated mixture of the mixed

plastics and cellulose samples in a similar ratio to the one found in the RDF, was prepared and analysed by TGA. This is presented in Figure 2d which shows 73.6% loss of volatiles from cellulose and 18.7% loss from the plastics. These results indicated that for the RDF sample used in this present study, the degradation pattern of its volatile content could be recreated by degrading an appropriate mix of cellulose and mixed waste plastics, thus giving a quick way of estimating the proportions of the biogenic and plastic fractions. The results above indicated that the pyrolysis of RDF is mostly as a result of the thermal degradation of the biogenic (cellulosic) and plastic fractions. Further investigations are necessary to determine the contributions of these fractions to the pyrolysis products, as well as what interactions if any, exist between the individual products of these fractions which may influence the pyrolysis products. However the results of such investigations will be presented in future work.

3.2. Results from varying the heating rate during pyrolysis of RDF

The pyrolysis of RDF just like biomass always yields three major product fractions: gases, liquids and solids [11]. However, the variation in the yields of these products with varying process conditions could help explain any possible interactions between the components of RDF during the pyrolysis runs. Controlling the pyrolysis heating rate is one way of investigating this effect [16].

3.2.1 Effect of heating rate on product yields

Table 2 shows the variations in the product yields when the RDF samples where pyrolysed at heating rates of 5, 20, 90 and 350 °C min^{-1} to a final temperature of 800 °C and held at this temperature for 20 min. The results suggest a definite trend of the product yields, with increasing heating rate at the process conditions defined by the reactor design. However, it is clear that no clear distinction could be made between the yields of products at 5 °C min^{-1} and

20 ℃ min^{-1} heating rates, indicating that much larger differences in heating rates is often required to significantly affect product yields. Gas yield increased from 14.4 to 46.9 wt % while oil yield decreased from 55 to 23 wt% with increasing heating rate. The solids residue showed a continuous decreasing trend in yield with increasing heating rate from 5 to 350 °C min^{-1}, probably as result of the thermal degradation of higher molecular weight hydrocarbons within the r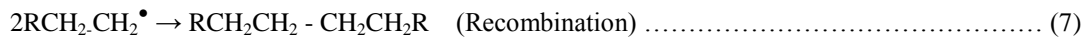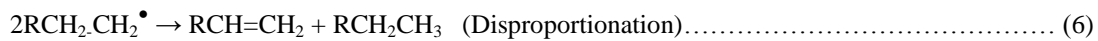esidue [17]. Marcilla et al [18] reported similar product yields for the slow and fast pyrolysis of HDPE in a fluidized bed. The higher gas yields and lower oil yields noted at the highest investigated heating rate compared to the lower heating rates yields, was as a result of the rapid secondary thermal cracking of the primary pyrolysis vapour. High heating rates and longer residence times combined with high temperatures have been reported to increase gas production from pyrolysis of waste [1, 19]. Due to the rapid heating rate, the pyrolysis vapours from the primary thermal decomposition of the RDF were released into the high temperature atmosphere, which when combined with the residence time estimated to be up to 9 sec in this reactor, initiated the secondary cracking of the vapours to yield lighter molecular weight hydrocarbons and more gases. Garcia et al. [9, 19] have investigated the effects of residence time on the pyrolysis of MSW and their work indicated that volatile residence times above 1 sec favours secondary pyrolytic cracking reactions which results in higher gas yields.

3.2.2 Gas composition

The effects of the different heating rates on the composition of the pyrolysis gas, in this present study, are also shown in Table 2. This shows an increase (on a mass basis) across the detected compositional fractions that make up the gas products, with increasing heating rate. The highest gas compositional mass yields were produced at the highest heating rate, suggesting the promotion of secondary thermal cracking. The degradation of polymers which occurs during pyrolysis has been explained to be as a result of free radical degradation via

different mechanisms: random scission, side group scission, monomer reversion and a combination of any [20]. For example during the pyrolysis of higher alkanes, the carbon-carbon bonds randomly cleave along the chain to produce smaller alkyl radicals [21]. The degradation mechanism or mechanisms which will be applicable during the pyrolysis of polymers are dictated by factors such as, the reaction conditions, the strengths of the chemical bond within the polymer and the stability of the resultant product molecule. Often the weakest chemical bonds are first cleaved but equally important is the fact that a bond is likely cleaved if such cleavage would produce stable products. However, depending on the reaction conditions, including heating rates, the sequence of likelihood of bond cleavage may be altered. The dTG in Fig. 2a shows that different reactions take place during the pyrolysis of RDF, with the main steps being drying and then the splitting of molecules. Essentially, during the pyrolysis of RDF at a heating rate of 350 °C min^{-1}, the reactions indicated by the first three peaks in Fig. 2a must have happened very quickly and in no definite order depending on the heat flux across the individual particles of RDF. Williams et al. [14] reported a merging of the degradation peaks for wood pyrolysis at higher heating rates. The occurrence of the three degradation peaks for the pyrolysis of RDF at almost the same time as a result of rapid heating, would introduce a different set of interactions for the pyrolysis products compared to pyrolysis at slow heating rates. At rapid heating rates, the initial products of the different degradation reactions during RDF pyrolysis were concurrently released into the hot reactor atmosphere where further thermal degradation and other reactions took place. Reactions such as auto-thermal gasification [22], the Boudouard reaction (Eqn.6.), methane dry reforming reactions (Eqn.7.) [23], recombination and disproportionation reactions [21] have been proposed for pyrolysis products.

$$C(s) + CO_2 \leftrightarrow 2CO \qquad Q = \text{-173.8 KJ mol}^{-1} \text{ (Boudouard reaction)}\text{………………………... (3)}$$

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad Q = \text{-247.3 KJ mol}^{-1} \text{ (Methane dry reforming)}\text{………..………….. (4)}$$

$CH_aO_b + (2 - b)H_2O \rightarrow (0.5a + 2 - b)H_2 + CO_2$ (Auto thermal biomass gasification)................ (5)

$2RCH_2\text{-}CH_2^{\bullet} \rightarrow RCH=CH_2 + RCH_2CH_3$ (Disproportionation)...................................... (6)

$2RCH_2\text{-}CH_2^{\bullet} \rightarrow RCH_2CH_2 \text{ - } CH_2CH_2R$ (Recombination) .... (7)
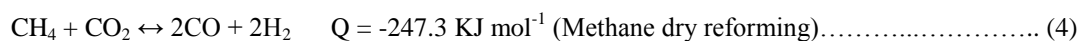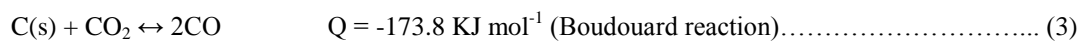
The complex combination of reactions and interactions during the rapid heating rate pyrolysis of RDF at high temperature, coupled with the secondary thermal cracking of the primary pyrolysis vapours, could result in a different gas composition compared to that attained for pyrolysis at lower heating rates as suggested by Table 2. The CO_2 content in the gas increased with the heating rate, and may be as a result of the promoted decomposition of carboxylic groups [24]. In addition, the yield of CO increased with increasing heating rate, and can be attributed mainly to the promoted secondary reactions [25, 26]. As can be clearly seen in the Table 2, the yield of CO was consistently lower than that of CO_2 at heating rates up to 90 °C/min, however at the heating rate of 350 °C/min the yield of CO became much higher than the yield of CO_2. Clearly, this suggested a significant change in the pyrolysis reactions. The trend in the yields of CO and CO_2 with increasing heating rate suggests the likely occurrence of Boudouard reaction at the heating rate of 350 °C/min. Although, dry-reforming [18] of hydrocarbons have been suggested to contribute to CO yields, in this study, the yields of methane and C_2-C_4 hydrocarbons increased consistently with increased heating rate. This would indicate a much less contribution to CO formation from dry-reforming. Table 2 also shows calorific values of the produced gases of between 12.5 and 24.8 MJ m^{-3}, with an increasing trend with respect to heating rate. This could be mostly due to more gases, especially CO, methane and C_2-C_4 hydrocarbon gases, being produced as a result of higher conversion of the volatiles to gases as well as solid-gas reactions at the elevated heating rates via secondary reactions.

3.2.3   Composition of liquid products

The liquid products from the pyrolysis of MSW is often very complex in nature [10, 27-29] and contains a mixture of oxygenated and non-oxygenated hydrocarbons. In order to investigate the effects of the heating rate on the pyrolysis liquid, the liquids from the pyrolysis of RDF at the different heating rates were analysed by GC/MS/MS. Since the yields of products from pyrolysis at 5 °C min^{-1} and 20 °C min^{-1} heating rates were similar, detailed analysis of the tar from the 20 °C min^{-1} heating rate is not presented in this present study. Figs. 3 and 4 show the chromatograms of the oil/tar products obtained from the pyrolysis of the RDF at 800 °C, using heating rates of 5 °C min^{-1} and 350 °C min^{-1}, respectively. The figures, especially for the run at 5 °C min^{-1} show that the analytical protocol adopted in this study to separate the aliphatics from the aromatic/oxygenates compounds was largely successful. This enabled the separate analysis of these fractions with minimal co-elutions and mis-identification of the compounds.

The results of the GC/MS/MS analysis are presented in Figures 3 and 4, which shows compounds detected from the liquids obtained from the pyrolysis of the RDF at heating rates of 5 and 350 °C min^{-1} respectively. The relative abundances of these compounds in the pyrolysis liquid are also shown. The chromatograms in Figures 3 and 4 show that compared to the lower heating rate pyrolysis, more aromatic compounds were detected and at higher concentrations in the oil obtained from the test at 350 °C min^{-1}.

The yields of organic compounds in the oil/tar samples at 5 °C min^{-1}, 90 °C min^{-1} and 350 °C min^{-1} heating rates are presented in Figure 5. Results show that the oil/tars contained much olefins than paraffins, resulting from the thermal cracking process of the plastics. There was a continuous increase in the yields of aromatic hydrocarbons and phenolic compounds with increasing heating rates. Figure 5 shows that in the liquid from pyrolysis at 5 °C min^{-1}, more alkanes, alkenes and oxygenates were detected compared to the pyrolysis at the highest heating rate. Miskolczi et al. [5] also detected the presence of alkanes and alkenes from RDF

pyrolysis at 550 °C. Phan et al. [27] detected increases in the presence of aromatics in the oil from waste pyrolysis at 700 °C. While Ates et al. [30] also reported an increase in the yield of single and multi-ringed aromatic groups with increasing temperature up to 800 °C from the pyrolysis of corncob. The predominance of aromatic hydrocarbons in the oil from pyrolysis at the highest heating as shown in Fig. 5 suggests that rapid heating rate pyrolysis caused an intensification of the high temperature effects, resulting in the formation of more aromatic compounds. The aromatic compounds are produced from reactions which involve initially the conversion of alkanes to alkenes, then the conversion of alkenes to monocyclic aromatic compounds via Diels-Alder cyclization reactions [31, 32], and finally the conversion of monocyclic compounds to polycyclic compounds. These reactions have been reported to be favoured by high temperature, long residence times and high heating rates. This would explain the predominance of aromatic compounds in the liquid from pyrolysis at 350 °C min^{-1} compared to the predominance of mostly alkanes and alkenes in the liquid from pyrolysis at 5 °C min^{-1}.

3.2.4 Characteristics of solid residues

Table 2 shows the effects of the different heating rates on the solid residues from the pyrolysis of RDF at 800 °C. During pyrolysis as the heating rate was increased from (5 to 350 °C/min), the solids yield showed a decreasing trend. This reduction suggests that higher heating rate influences the solids yields [14] by encouraging the complete degradation and release of any trapped volatiles within the solid residue structure. The GCV of the solid product from the lower heating rate pyrolysis is higher at 18.45 MJ Kg^{-1}, compared with a CV of 16.37 MJ Kg^{-1} for the higher heating rate as shown in Table 2. This difference could be as a result of lower ash content per mass basis [27] and residual volatile matter within the structure of the pyrolysis solid produced from the lower heating rate process. This difference could also be as a result of the Boudouard reaction which is expected to become significant

during higher heating rate pyrolysis. Table 2 also shows the BET surface area for the solid products and indicates that the solids from the lower heating rate pyrolysis, has a higher surface area (170 m^2g^{-1}) than that for the solids from pyrolysis at 350 °C min^{-1} (84 m^2g^{-1}). This suggests that during the rapid heating rate pyrolysis, the thermal shock impacted on the RDF sample caused the volatiles to be violently released from the RDF structure, thereby destroying the internal pore structure [33] and reducing the porosity of the solid product, compared to the slow pyrolysis where the volatiles gradually exit the structure of the RDF.

3.3   Effects of final pyrolysis temperature

The effect of the different final pyrolysis temperatures investigated on the product yields from RDF pyrolysis is shown in Table 3. These tests were carried out at rapid heating rates, to the final temperatures of 700, 800 and 900 °C. A careful look at the tabulated results reveals a trend in the product yields with increasing temperature. Essentially the oil and solid yields decreased while the gas yield increased with increasing temperature. Similar trends in product yields with increasing pyrolysis temperature have been reported by other researchers as well [15, 34-38]. At 800 °C the gas yield increased to 46.9 wt% from 43.6 wt% at 700 °C as result of cracking of larger molecules in the oil products (Table 3) to increase the yields of CH_4 and C_2-C_4 in the gas products at this temperature. However, increasing the temperature to 900 C, led to a decrease in the yields of the hydrocarbon gases possibly due to other secondary gas-phase reactions including cracking reactions and CO_2 drying reforming. At 900 °C, the gas yield increased to 52.3 wt%, solids yield reduced to 21 wt%, while the tar yield remained apparently unchanged at 23 wt%. It appears that the increased gas yield at 900 °C was therefore mostly due to further degradation of the solids at such high temperatures. The further degradation of the solids fractions of MSW at such temperatures have been linked to the degradation of inorganics especially $CaCO_3$ contained in MSW, into CaO and CO_2 [9, 19]. This may also be responsible for some of the increase in CO_2 recorded in the gas

composition from pyrolysis at 900 °C, and subsequently for the reduction in the CV of the produced gas since CO_2 has no calorific value. The reduction in the gas CV could also be as a result of reduced amount of hydrocarbons, especially $C_2 - C_4$ gases at this temperature, indicating possible thermal cracking of these gases at the higher temperature of 900 °C. The CV of the gas product at 800 °C was the highest at 24.8 MJ m^{-3}, indicating that this might be a good temperature for optimum gas production from RDF rapid pyrolysis at the conditions stipulated by the reactor in this study.

4.0   Conclusion

Pyrolysis of RDF as a representative of MSW has been carried out in a horizontal tubular reactor where different process parameters were varied, such as the; heating rate and final pyrolysis temperature of the sample, in order to investigate their effects on the product yields and compositions. TGA analysis of RDF, cellulose and mixed waste plastics indicated volatile degradation at two temperature zones similar to the degradation temperatures of cellulosic and plastic content. Hence the biomass (cellulosic) and plastic contents of RDF could be roughly estimated by the analysis of volatiles degradation in its TGA and dTG thermograms. Increasing the heating rate and final temperature resulted in an increased gas yield, reduced liquid yield and reduced solids yield at the conditions investigated. The calorific value of the product gas was also found to increase with increasing heating rate. FTIR and GC/MS/MS analysis showed that the liquid from rapid pyrolysis was found to contain mostly aromatic compounds which could be formed from the conversion of alkanes to alkenes and then to monocyclic aromatics via Dies-Alder reactions and finally to polycyclic aromatics. On the other hand the liquid from slow pyrolysis was found to contain mostly alkanes, alkenes and oxygenates. The solids from slow pyrolysis gave a slightly higher CV than that from rapid pyrolysis. Rapid pyrolysis of RDF at 800 °C with a long

residence time was the optimum process condition for gas production as it produced the gas yield with highest calorific value of 24.8 MJ m^{-3}. Such conditions are easily achievable using a fluidized bed reactor with small and closely uniform RDF feed sizes, due to high heat transfer rates and good mixing properties of this reactor as well as better heat transfer properties of smaller sized particles.

Acknowledgements

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