THERMAL DECOMPOSITION AND GASIFICATION OF BIOMASS PYROLYSIS GASES USING A HOT BED OF WASTE DERIVED PYROLYSIS CHAR

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ABSTRACT

Chars produced from the pyrolysis of different waste materials have been investigated in terms of their use as a catalyst for the catalytic cracking of biomass pyrolysis gases during the two-stage pyrolysis-gasification of biomass. The chars were produced from the pyrolysis of waste tyres, refused derived fuel and biomass in the form of date stones. The results showed that the hydrocarbon tar yields decreased significantly with all the char materials used in comparison to the non-char catalytic experiments. For example, at a cracking temperature of 800 °C, the total product hydrocarbon tar yield decreased by 70% with tyre char, 50% with RDF char and 9% with biomass date stones char compared to that without char. There was a consequent increase in total gas yield. Analysis of the tar composition showed that the content of phenolic compounds decreased and polycyclic aromatic hydrocarbons increased in the product tar at higher char temperatures.

Key words: Tar; Bio-oil; Biomass; Waste; Pyrolysis

1. Introduction

There is increasing worldwide concern in relation to the use of fossil fuels and the associated emissions of greenhouse gases. The thermochemical conversion of biomass, as a renewable source of energy has received increased interest since it is considered as a viable and sustainable alternative source of energy supply (Sun et al., 2011). One of the most promising biomass conversion processes is gasification in which the complex biomass hydrocarbons are thermally degraded into useful gaseous species, mainly hydrogen, carbon dioxide and carbon monoxide (Machin et al., 2015). However, one of the main issues associated with biomass gasification is tar formation in the syngas. Tar is a chemically complex mixture of aromatic hydrocarbons and oxygenated hydrocarbons and is normally defined as molecular weight hydrocarbons greater than benzene (MW >78) (Maniatis and Beenackers, 2000; Suzuki et al., 1992; Devi et al., 2003) . However, tars have been reported (Brage et al., 1996) to have molecular weights of over 500 and it is the higher molecular weight compounds with high boiling points which represent the technical issue associated with the tar content of syngas. Tars can condense in the process equipment causing blockage of pipelines and downstream syngas utilisation systems such as engine and turbine fuel lines and injector nozzles. Therefore, various methods have been investigated for tar removal, including thermal cracking, catalytic cracking and physical treatments. Among these methods, the catalytic cracking process is efficient in terms of high tar conversion and the production of mostly tar-free gas with high heating value. Various catalysts have been extensively investigated for tar reduction during the biomass gasification process, including alkali metals (Suzuki et al., 1992), zeolites (Dou et al., 2003), nickel based catalysts (Li et al, 2009; Cheah et al., 2013; Kimura et al., 2006) etc. The main problems associated with the use

of such catalysts are the high cost, difficulty of regeneration and the deactivation by coke deposition on the catalyst.

The use of carbonaceous char at high temperature (500 – 800 °C) to act as a catalyst for tar decomposition has been investigated by several authors (Sun et al., 2011; Phuphuakrat et al., 2010; Gilbert et al., 2009; Wang et al, 2011; Shen et al., 2014; Chang et al., 2003). The process conditions most commonly used for catalytic tar reduction involve temperatures between 800 and 900 °C in an atmosphere of steam and CO_2 (Abu El-rub et al, 2008). For example, Abu El-Rub (2008) investigated the decomposition of tar model compounds using biomass pyrolysis chars in comparison with conventional tar removal catalysts in the presence of steam and CO_2 and in relation to temperature. They showed that at 900 °C, the conversion of phenol was mainly through thermal cracking, but naphthalene decomposition involved catalytic cracking. The biomass derived pyrolysis chars were shown to be effective for the conversion of the model tar compounds. Zhao et al (2015) used a two-stage pyrolysis-gasification reactor to investigate a range of process conditions for the removal of tar from the pyrolysis of rice straw using biomass char produced from the pyrolysis of the rice straw. They investigated the influence of different reforming agents, CO_2, H_2O or O_2 introduced into the second stage reactor and different char temperatures of 700 to 1000 °C. They reported that a higher temperature of char bed eliminated more of the tar and that the presence of steam was the most effective for tar removal compared to the other reforming agents. Zhao et al (2015) reported that in the absence of reforming agent, where catalytic cracking of tar over the char bed occurred; significant removal of tar was reported, for example 85% tar conversion at 700 °C rising to 95% at 900 °C.

To further understand the role that char plays in tar reduction, it is of interest to investigate the reactions of biomass pyrolysis gases over a bed of pyrolysis char at high temperatures. Sun et al. (2011) investigated the use of high temperature char for the decomposition and

gasification of biomass pyrolysis gases in a separate hot char reactor at temperatures between 500 and 700 °C using biomass char. Similarly Gilbert et al. (2009) used a two-stage reactor system using char for the for cracking of biomass pyrolysis gases. Pyrolysis of biomass produced pyrolysis gases which were then subsequently thermal cracked over a hot bed of char between 500 and 800 °C.

Where biomass pyrolysis is involved, inevitably there is the formation of steam through autogeneration, formed from the release of moisture, but also as a reaction product from pyrolysis of the biomass. Pyrolysis will also produce significant concentrations of CO_2. Therefore, although pyrolysis and char cracking may take place in an inert atmosphere of nitrogen or argon (Sun et al., 2011; Gilbet et al., 2009), the pyrolysis of biomass will produce a partial oxidation atmosphere through the formation of steam and CO_2 as reaction products which can react with the char to produce CO, CO_2, H_2.

Guoxin and Hao (2009) showed that biomass moisture content can autogenerate a steam atmosphere which can react with biomass pyrolysis gases to produce increased reaction between the evolved intermediate products of pyrolysis due to the reforming of tar, methane and higher hydrocarbons, via reforming reactions and the water gas shift reaction. They found that the highest reaction was found with fast heating rates where the evolved autogenerated steam could react with the pyrolysis gases due to the fast drying and pyrolysis gases occurring over shorter residence times compared to slow heating rates. High moisture content of the biomass was found to directly correlate with higher hydrogen production. In addition, autogenerated steam would be derived from the product water from the pyrolysis of the biomass in addition to the release of moisture during drying. The presence of a downstream hot char bed at temperatures between 700 and 900 °C would provide a further zone for thermal and catalytic degradation of tar and higher hydrocarbons, together with

autogenerated steam char gasification reactions and also steam reforming reactions of the pyrolysis tar and hydrocarbons.

In this work, the effectiveness of using different pyrolysis char materials derived from the pyrolysis of waste materials have been investigated for tar cracking during the two-stage pyrolysis-gasification of biomass using a bench scale fixed bed reactor at char temperatures of 600 to 800 °C. The chars were obtained from the pyrolysis of waste tyres, municipal solid waste processed to produce refuse derived fuel (RDF) and biomass wastes in the form of date stones. The influence of char catalytic cracking temperature on gas composition and tar composition was investigated.

2. Materials and methods

2.1 Materials

Wood pellets produced from waste wood with a particle size of ~1.0 mm were used as the raw material for the pyrolysis which generated the pyrolysis gases for subsequent cracking in the hot bed of char. The proximate analysis of the wood pellets gave 75.0 wt.% volatiles 7.0 wt.% moisture 2.0 wt.% ash and 15.0 wt.% fixed carbon. Elemental analysis of the pellets gave 46.0 wt.% carbon, 5.6 wt.% hydrogen, 0.7 wt% nitrogen and 45.7 wt% oxygen (by difference).

The waste tyre sample used to prepare the tyre derived char was a shredded mixture of waste truck tyres. The steel reinforcement in the tyre was removed followed by shredding and sieving. Refuse derived fuel (RDF) was used as a representative sample of municipal solid waste with the elimination of recyclable materials such as metals and glass. The RDF sample was carefully prepared from 2 kg of RDF and was mixed, coned and quartered and

further shredded to enhance homogeneity. The biomass waste sample was in the form of date stones which were obtained from Oman. All the samples were ground and sieved to a particle size of 1 mm. Table 1 shows the properties of the waste materials used to prepare the chars.

2.2 Pyrolysis reactor

The pyrolysis chars were produced using three different waste materials in the form of waste tyre, RDF and biomass (date stones). Pyrolysis of the wastes was carried out in a fixed bed reactor, externally heated by an electrical furnace (Figure 1(a)). The waste (10 g) was placed in a sample crucible within the reactor. The pyrolysis temperature programme was, heating at a rate of 10 ℃ min^{-1} to a final temperature of 800 ℃ and held at that temperature for one hour. Nitrogen was used as the carrier gas. A condenser system consisting of a water-cooled and dry ice-cooled condensers was used to trap the condensable liquids. The chars recovered from the pyrolysis reactor after the experiment were ground and sieved to a particle size of ~1mm and dried overnight at a temperature of 105 ℃. The reproducibility of the experimental system was ensured via repeat experiments. For example, several repeated experiments with biomass in the absence of char (where sand was used) gave a standard deviation on char recovered mass of 0.4 wt.%, for liquid 0.7 wt.% and gas yield of 2.1 wt.%. Gas compositional analysis for the same repeated experiment gave a standard deviation for CO of 3.9 Vol.%, H_2 of 1.3 Vol.%, CO_2 of 1.7 Vol.%, CH_4 of 2.2 Vol.% and $C_2 - C_4$ of 5.5 Vol.%.

2.3 Tar decomposition using pyrolysis chars

The use of waste derived pyrolysis chars for bio-oil/tar catalytic cracking was investigated in a two-stage fixed bed reactor made of stainless steel with an inner diameter of 22 mm and a length of 160 mm and was fully instrumented with monitoring and control of gas flow and temperature. A schematic diagram of the reactor is shown in Figure 1(b). The first stage involved pyrolysis of the wood pellet biomass and the second stage contained the waste derived pyrolysis chars maintained at a temperature of either 600 °C, 700 °C or 800 °C. The two-stage reactor system was continually purged with nitrogen. Further experiments were undertaken using a biomass:tyre char ratio (1:1 – 1:3) on the conversion of tar from the pyrolysis gases produced from the pyrolysis of the biomass waste wood pellets.

The experiments consisted of the initial heating of the second stage hot char reactor to the desired temperature at a heating rate of 40 ℃ min^{-1}. Once the temperature of the char reactor was stable, the first stage pyrolysis reactor was heated at a rate of 40 ℃ min^{-1} to a final temperature of 500 °C. The evolved pyrolysis gases, including tar, higher hydrocarbons, product autogenerated steam and non-condensable gases such as methane, ethane etc. hydrocarbons, carbon dioxide and carbon monoxide were passed directly to the hot char reactor where the range of gasification, reforming, thermal and catalytic cracking reactions occurred. Experiments were also undertaken in the absence of char for comparison,. The product gases were passed to a series of dry ice condensers where condensable tar/bio-oil and water were condensed. The uncondensed gases were collected in a Tedlar™ gas sample bag. After the experiment, the gases were analysed using gas chromatography and with the known flow rates and molecular mass of each gas, the total mass of gases could be determined. The pyrolysis char from pyrolysis of the biomass wood pellets was collected from the first stage pyrolysis reactor and weighed. The liquid products collected in the condenser system were weighed and then separated into a hydrocarbon oil/tar fraction and water fraction using Karl Fischer titration with a Metrohm 890 Titrando analytical system.

The collected gaseous products were analysed off-line by packed column gas chromatography (GC). The permanent gases (N_2, H_2, CO, CO_2) were analysed using a Varian CP-3380 GC with two separate columns, each one with a thermal conductivity detector, where H_2, CO, O_2 and N_2 were analysed on a column packed with 60-80 mesh molecular sieve with argon carrier gas, while CO_2 was analysed on 80-100 mesh HayeSep column. A separate Varian CP-3380 GC with an 60-80 mesh column and a flame ionization detector (FID) analysed the $C_1 - C_4$ hydrocarbons using N_2 as carrier gas with a HayeSep GC column.

2.4 Tar analysis

The composition of the condensed product bio-oil/tar was analysed for the main hydrocarbon and oxygenated hydrocarbon compounds present using coupled gas chromatography-mass spectrometry (GC-MS). Before GC-MS analysis the product bio-oil/tar was dried by passing through a sodium sulphate column. The GC-MS used was a Varian CP-3800 GC connected to a Varian Saturn 2200 MS. An aliquot (2 µl) of the bio-oil/tar dissolved in dichloromethane solvent for analysis. The GC injector port was at a temperature of 290 °C; the GC analytical programme was 40 °C for 2 min; 40 to 280 °C at 5 °C min^{-1}; 280 °C for 10 min. The GC to MS transfer line was at a temperature of 280 °C and the ion trap was at 200 °C.

2.5. Char characterisation

The physical properties of the waste tyre derived char, RDF pyrolysis char and biomass date stones pyrolysis char materials including BET surface area and porosity were determined

by the adsorption of N_2 at 77K using a Micromeritics TriStar 3000. Before analysis, the samples (0.1 g) were degassed under Nitrogen for 3 h at 250 °C. The micropore volume used the Dubinin Radushkevich (DR) and the mesopore volume used the Barret-Joyner-Halenda (BJH) methods of data analysis. Pore size distribution was obtained by the Density Functional Theory (DFT) method.

Proximate analysis of the char samples was carried out using the thermogravimetric analysis (TGA) method under nitrogen (to determine moisture and volatiles) and air atmosphere (to determine ash). Elemental analysis was carried out with a CE Instruments Flash EA2000. The results are shown in Table 2.
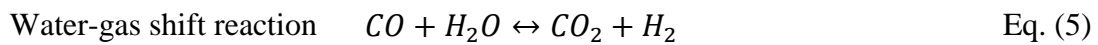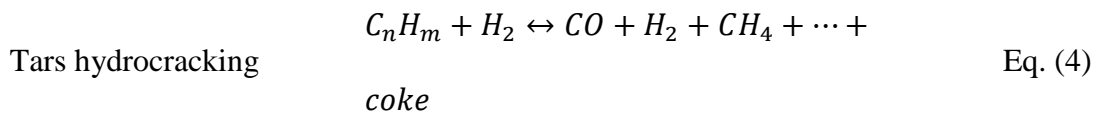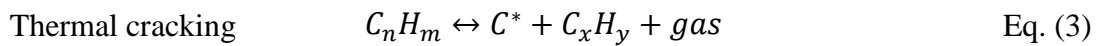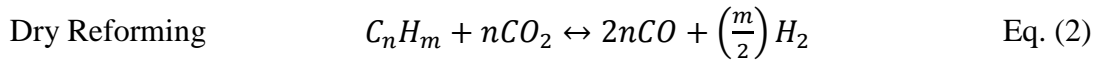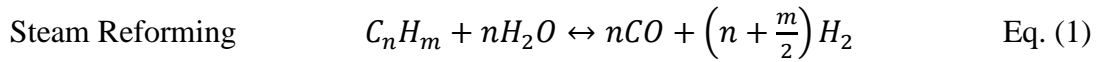
3. Results and discussion

3.1 Biomass pyrolysis gas conversion using waste derived pyrolysis chars

The waste derived pyrolysis chars produced from waste tyres, RDF and date stones were investigated for their effectiveness in the conversion of biomass pyrolysis gases including the heavier molecular weight hydrocarbons (tar) from the pyrolysis of biomass, waste wood pellets. The results are presented in Table 3. For comparison, the results without char are also presented where sand was substituted for the waste char sample. In Table 3, the char yield represents the residual yield of char in the first stage pyrolysis reactor produced from the pyrolysis of the biomass wood pellets. The biomass pyrolysis char yield was always ~24wt.%, since the pyrolysis of the biomass was always from ambient temperature to 500 °C and the process would be unaffected by the reactions downstream of the evolved pyrolysis gases with the hot bed of char.

In the absence of char, the tar yield decreased with an increase in the second stage char cracking temperature from 28.0 wt.% at 600 °C to 15.3 wt.% at 800 °C. It can be observed from Table 3 that the tar yields decreased significantly with all the waste char derived materials used in comparison to the experiments without char. The tyre derived pyrolysis char produced the largest conversion of the biomass tar to gas, reducing the condensed bio-oil/tar from 14.8 wt.% tar at 600 °C to 4.6 wt.% at 800 °C with a corresponding increase in gas yield from 31 wt.% at 600 °C to 57.5 wt.% at 800 °C. The RDF char and biomass date stones char producing lower conversion of bio-oil/tar, for example 7.6 wt.% and 13.9 wt.% tar respectively at 800 °C. Under the same studied experimental conditions, at a char cracking temperature of 800 °C, the total bio-oil/tar yield decreased by 70, 50 and 9% with tyre, RDF and date stones char respectively compared to that without char.

The product liquid collected in the condensers was a mixture of a pale yellow coloured oil and water. The condensed water produced from the pyrolysis of the biomass and from the moisture content of the biomass decreased with increasing second stage (sand) temperature (Table 3). This was also the case when each of the waste derived chars was introduced into the second stage cracking reactor, but to a greater extent. The data shown in Table 3 show the total liquid yield and also the yield of water and tar in the liquid as determined from the Karl Fischer analysis. These results showed that char has a significant catalytic effect in reducing the total tar yield during the biomass-gasification of biomass. The catalytic activity of char produced from biomass for tar removal has been studied by Gilbert et al. (2009). The investigated char was effective in enhancing heavy tar cracking in a fixed bed reactor but not to such a high degree as found in this work. Abu El Rub (2008) reported about 85 % removal of naphthalene by biomass char, however the same char could remove only 58% of real biomass produced tar.

An increase in the total gas yield was observed with the introduction of char in the second stage reactor (Table 3). For example, at a char cracking temperature of 800 °C, the highest gas yield (59.5 wt.%) was obtained with the use of RDF char while date stones char produced the lowest yield (50.6 wt.%). The analysis of the produced gases showed that the main gas concentration that increased, was that of hydrogen. Cracking of the bio-oil/tar hydrocarbons would produce a range of lower molecular weight hydrocarbons, including methane and C_2—C_4 hydrocarbon gases and also hydrogen. As shown before (Table 3), the tar yield is decreased with an increase in char temperature from 600 to 800 °C. The production of hydrogen could also be from autogeneration of steam and subsequent reactions of the steam with the generated biomass pyrolysis hydrocarbons and the waste derived char through gasification, water gas shift, methanation and reforming reactions (Abu El-rub et al., 2004; Devi et al., 2005);

Steam Reforming	$C_nH_m + nH_2O \leftrightarrow nCO + \left(n + \frac{m}{2}\right)H_2$	Eq. (1)
Dry Reforming	$C_nH_m + nCO_2 \leftrightarrow 2nCO + \left(\frac{m}{2}\right)H_2$	Eq. (2)
Thermal cracking	$C_nH_m \leftrightarrow C^* + C_xH_y + gas$	Eq. (3)
Tars hydrocracking	$C_nH_m + H_2 \leftrightarrow CO + H_2 + CH_4 + \cdots +$ $coke$	Eq. (4)
Water-gas shift reaction	$CO + H_2O \leftrightarrow CO_2 + H_2$	Eq. (5)

(C_nH_m hydrocarbons representing tars. C_xH_y hydrocarbons representing lighter tar)

Sun et al. (2011) investigated the effects of using charcoal as a catalyst for tar reduction and observed an increase of H_2 and CO_2 yields with 3.9 and 2.9% compared to that without charcoal. The authors attributed the increase of H_2 and CO_2 to the auto- generated steam gasification of char.

3.2 Tar Composition

The composition of the condensed bio-oil/tar products from the pyrolysis of biomass in the presence of the tyre char, RDF char and date stones char at the hot char reaction temperature of 800 °C were analysed using GC-MS. Figure 2 shows the total ion chromatograms for the bio-oil/tar collected after passing through the waste derived tyre, RDF and date seed chars and compared to the bio-oil/tar in the absence of char (with sand as a blank). The main compounds detected were phenolic compounds and polycyclic aromatic hydrocarbons (PAH). The relative peak area was calculated in proportion to the total peak area found with the oil produced with the experiment where no char was present in the second stage. Figure 3 shows the total phenolic compounds and PAH for each of the bio-oil/tars in relation to each of the waste cracking chars at a char temperature of 800 °C. The results obtained from the non-catalytic experiment are presented for comparison.

The oxygenated phenolic compounds decreased with all the waste derived char materials compared to the experiment in the absence of char. In particular, the presence of the RDF char produced the lowest concentration of phenolic compounds in the condensed bio-oil/tar. With regard to the fraction of polycyclic aromatic hydrocarbons in the bio-oil/tar at a cracking temperature of 800 °C (Figure 3), the fraction decreased significantly with the use of tyre char but was higher with the date stones char compared to the experiment without char. The presence of the biomass char seems to promote the cyclization, aromatization and condensation reactions that lead to the formation of PAHs. The porosity and the acidity of samples could play a role in affecting the product distribution of the produced oil. The acidic properties of the catalytic materials have a significant role during pyrolysis catalytic processes. The acidic sites have been found to induce the isomerization, cracking and

aromatization reactions. The activity of alumino silicate materials for oil cracking and conversion of large hydrocarbons have been found to depend greatly on the strength of their acidic groups. The materials with moderate acid strength present a higher activity than the classical silica-alumina catalysts (Beck et al, 1992). Iliopoulou et al. (2007) investigated the catalytic pyrolysis of biomass using mesoporous alumina silicate materials with various acidity, the material with the higher number of acidic groups reduced the organic phase of the liquids products by 55% compared to the material with less acidic groups. The authors concluded that the materials with a higher acidity induced higher concentrations of phenols compared to the non-acidic materials. Additionally, it has been found that increasing the number of acid sites of catalysts led to a decrease of the PAHs compared to the untreated sample. Thus the difference in the catalytic activity of the studied char materials for tar reduction could be due to the difference of their surface chemistry and their acidic and basic groups. The tyre char had a higher number of acidic groups than date stones and RDF char which were found to be basic in nature. (Al-Rahbi et al., 2015).

The high ash content of tyre and RDF char compared to that of date stones char (Table 2) could be another reason for the low activity in conversion of bio-oil/tar hydrocarbons for the biomass date stones char. For comparison, in separate experiments, wood char with an ash content of 2% has been investigated for bio-oil/tar removal at the studied conditions at a char cracking temperature of 700 °C. It was found that wood char had a lower bio-oil/tar cracking activity than the other types of char used in this study (results not shown here). The ash composition and the type of metal present in the ash could play a role in enhancing tar reduction due to catalytic effects. The significant reactivity of tar with tyre char could be due to the catalytic effects of the minerals such as Zn, which was present in quite a high percentage of 2.95 wt.% for the raw tyre sample used in this work (Al-Rahbi, et al., 2015). For example, in the study by Oztas and Yurum (2000), coal samples were impregnated with

several metals including Zn. The author observed some catalytic effect of Zn and Ni in decomposing many of the tar compounds. Direct correlation between the porosity, acidic properties and metal species and the oil product yields during pyrolysis-reforming of biomass would need further study (Iliopoulou et al., 2007).

For the tyre char sample, the influence of char cracking temperature from 600 °C to 800 °C was investigated in terms of the change in bio-oil/tar composition after passing through the hot bed of char. The condensed tar compounds formed during the pyrolysis-gasification of biomass were identified quantitatively using GC-MS. The effect of temperature on tar reduction with the use of tyre char is shown in Figure 4. The tar compounds were divided into phenols, 1-ring, 2-ring and 3-4 rings PAH. The results show that char cracking temperature plays a significant role in decomposing and changing the bio-oil/tar composition. At the temperature of 600 °C, oxygenated phenolic compounds contribute nearly 100% of the total tar, whereas with increasing cracking temperature to 800 °C, PAHs with 2-4 rings are the dominant compounds. At 700 °C, the main tar compounds were alkyl- substituted PAHs. However, these compounds were shifted to non-substituted PAHs at 800 °C such as naphthalene, pyrene, flourene. A large decrease was observed in the number of the detected compounds at 800°C.

The results showed that increasing the cracking temperature led to the formation of PAHs. With the use of tyre char, less PAHs were detected in the condensed tar, the total PAH tar amounts decreased from 8171 µg g^{-1} to 3842 µg g^{-1} at a cracking temperature of 800 °C. However, the reduction of PAHs was accompanied with an increase of single ring compounds. For example, toluene and styrene were found to increase with the use of tyre char at 700 °C. This is could be attributed to the catalytic effect of tyre char in decomposing the higher molecular weight hydrocarbons into lighter compounds which then by Diels-Alder reaction resulted in the formation of styrene and toluene.

With regards to PAH, naphthalene is one of the compounds that have been found to be abundant in tar and is often used as a representative tar compound. According to some studies (Abu El-rub et al, 2008; Devi et al., 2005), various types of catalysts have been tested for naphthalene reduction. For example, In the study by Devi et al., (2005) the effectiveness of olivine and dolomite for naphthalene conversion has been examined at a temperature of 800 °C. The tar conversion was found to be 25% and 0% for olivine and dolomite respectively (Devi et al., 2005). In this study, at a cracking temperature of 700 °C, naphthalene contributed 12% and 26% of the oil composition with and without tyre char respectively. It is important to note that at cracking temperature of 700 °C the naphthalene concentration was found to increase with the use of tyre char compared to the experiment without char. This is could be due to the decomposition of heavy molecular weight PAHs with 3 & 4 ring producing smaller molecules such as naphthalene. With increase in the temperature to 800 °C, a marked decrease in naphthalene concentration was observed when tyre char was used, the decrease was about 67%. According to Jess (1996) the thermal decomposition of naphthalene starts at 1100-1200 °C . However, in this study the use of tyre char reduced the temperature requirement for naphthalene conversion by reducing the amount by 67% at 800 °C. PAH compounds with 3-4 ring including flourene, phenanthrene, folouranthene and pyrene were shown to increase markedly with increasing the bed temperature to reach the highest concentration at 800 °C and contribute to about 50% of the total tar yield in the absence of char catalyst. Tyre char was effective in reducing these compounds to about 70% compared to the experiment without char.

The samples were deficient in toluene and benzene; these compounds are volatile and could be lost during the oil preparation. However, these compounds are not considered as problematic tar compounds.

3.4. Char characterization

The BET surface area and the porous properties of the fresh and used waste derived char samples are shown in Table 4. A decrease in the BET surface area was observed for all the char materials after reaction with the biomass pyrolysis gases. The decrease was more marked for the RDF derived pyrolysis char. The decrease in BET surface area of the tyre derived pyrolysis char was less than that of the biomass date stones. Additionally, there was a 10, 80 and 20% decrease in the measured pore volume of the tyre char, RDF char and date stones char. The decrease in BET surface area of the chars after the char-tar reaction could be attributed to the deposition of high molecular weight tar compounds on the char surface, followed by condensation and polymerisation to form coke. Boroson et al. (1989) also reported a decrease in the surface area of chars due to deposition of tar onto the surface of the char during the cracking of wood pyrolysis tars over a hot bed of biomass char. A similar observation was reported by Zhao et al. (2015).

The porous texture of tyre char could have an influence on the tar conversion during pyrolysis/reforming of biomass via enhancing the bio-oil/tar decomposition reactions due to the presence of mesopores in the tyre char. The larger mesopores as opposed to micrpores encourages the bio-oil/tar compounds to enter the pores and thereby extend the residence time of tar cracking (Shen and Yoshikawa, 2014). According to the literature, an activated carbon with mesoporous texture has been found to enhance the decomposition of heavy molecular compounds into lighter products (Xu et al., 2009).

Abu El-Rub et al. (2008) reported that tars can be adsorbed on the active sites of the char material. The decomposition of tar over char materials is reported to be due to different mechanisms including deposition, dehydrogenation in which soot is formed over the char surface, and gasification of soot (Hosokai et al., 2008; Hosokai et al., 2011). The coke

formation and the gasification of the char have been found to occur simultaneously in which the gaseous products are formed due to these two processes (Hosokai et al, 2008). To further study the mechanism involved with the use of char for the tar decomposition, volatiles from the pyrolysis of biomass were reformed using charcoal with the presence of steam as a gasifying agent (Hosokai et al., 2011). The heavy tar was found to decrease from about 25% to 3% with the char, accompanied by consumption of steam as a result of the tar reforming over the char and gasification of the char.

Coke/carbon deposition produced from the aromatic compounds can be formed on the char surface due to the tar decomposition which has been found to decrease the porosity of the carbonaceous material. Hosokai et al. (2008) investigated the decomposition of benzene and naphthalene over charcoal and concluded that the decomposition of tar over char was mainly due to the coking rather than decomposition of aromatic compounds. In addition, the accumulation of coke on the surface of the chars may block the available active sites (metal species in the char) thus decreasing the char activity with time (Sueyasu et al., 2012). As a consequence, the BET surface area and the pore volumes of the tested char were decreased. However, coke formation on the char surface could not be observed during examination of the used char surfaces after reaction using scanning electron microscopy. The deactivation of char, due to pore blocking, is not considered as a serious problem as the spent char can be used a solid fuel (Abdullah and Wu, 2009).

3.5 Influence of the biomass to char ratio

Further experiments were undertaken with the tyre derived pyrolysis char to determine the influence of increasing the mass of char in the second stage hot char reactor in relation to the mass of biomass pyrolysed in the first stage section of the two-stage reactor. Experiments

were undertaken at a hot char temperature of 700 °C and at biomass to char ratios of 1:1, 1:2 and 1:3. The results in terms of product yield and gas composition are shown in figure 5(a) and 6(b) respectively. The results show that as the amount of char was increased in the tar cracking second stage reactor, the yield of condensed water and bio-oil/tar was significantly reduced from ~20 wt.% to 15 wt.% for the water and from 5 wt.% to <1 wt.% for the bio-oil/tar. In a study carried out by Gilbert et al. (2009), the heavy condensable phase was found be resistant to decomposition with an increase in the amount of char, whereas the light oil fraction showed a decrease with increasing the char amount. As the bio-oil/tar decreased, there was a corresponding increase in gas yield as the biomass to char ratio increased from 1:1 to 1:3. With a higher char amount, the pyrolysis vapour has a longer interaction time in the char bed resulting in cracking of the tar compounds to gaseous species particularly H_2 and CO (Figure 5(b)).With the increase of biomass to char ratio from 1:1 to 1:3, the H_2 concentration increased from 23.5 vol.% to 28 vol.%. Figure 5(b) also shows that the CO concentration decreased and the CO_2 concentration increased as the biomass:char ratio was increased, suggesting that autogeneration of steam was producing increased hydrogen and carbon dioxide through the water gas shift reaction. The hydrocarbons also showed a small decrease suggesting reforming of the product hydrocarbon pyrolysis gases.

4. Conclusions

Chars produced from the pyrolysis of waste materials have been used for the cracking of biomass derived pyrolysis gases during the pyrolysis-catalytic (char) gasification of biomass. Waste derived chars were effective in reducing the condensable bio-oil/tar hydrocarbons with tyre char proving the most effective producing a 70% reduction in bio-oil/tar yield compared to that without char. The results suggest that tar removal by char materials is mainly due to

the catalytic conversion and physical adsorption of tar compounds. The performance of chars in this study for tar removal was ordered as tyre char> RDF char> date stones char>no char.

Acknowledgements

5. References

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Table 1.

Composition of the raw waste materials.

Analysis (wt.%)	Tyre	RDF	Date Stones
Proximate analysis			
Volatiles	62.2	72.0	18.2
Moisture	1.3	5.0	7.5
Ash	7.1	11.0	4.0
Fixed carbon	29.4	13.	69.9
Ultimate analysis			
Carbon	81.2	47.5	46.2
Hydrogen	7.2	6.6	5.8
Nitrogen	0.5	0.9	0.8
Sulphur	2.6	0.0	0.0

Table 2.

The ultimate and proximate analyses of the waste derived char samples

	Tyre char	RDF char	Date stones char
Proximate analysis (wt.%)			
Volatiles	2.0	4.5	3.95
Fixed carbon	78.8	48.3	85.5
Ash	18.9	44	5.5
Ultimate analysis (wt.%)			
Carbon	70.06	44.77	85.67
Hydrogen	0.28	0.38	0.57
Nitrogen	0.83	1.08	2.25
Sulphur	4.78	0.49	0.11
Oxygen (by difference)	5.15	9.28	5.9

Table 3.

Influence of waste derived pyrolysis char on the product yield from the pyrolysis –gasification of biomass

	Without char			Tyre char			RDF char			Date stones char		
Temperature (°C)	600	700	800	600	700	800	600	700	800	600	700	800
Residual Biomass Char (wt.%)	24	23.5	23	24.5	24.5	23.5	24	24	23.5	24	23	24
Liquid (wt.%)	49	36	28.5	34	25.5	8.5	43.5	25.5	17	45.5	40.5	24.5
Tar (wt.%)	28	20.1	15.3	14.8	4.7	4.6	25.1	9.2	7.6	26.1	21.5	13.9
Water (wt.%)	21	15.9	13.3	19.15	20.8	3.9	18.4	16.3	9.4	19.15	19	10.6
Gas yield (wt. %)	22.4	33.5	46.6	31	41	57.5	33	44.3	59.5	26.3	38.75	50.6
Gas composition (vol%)												
CO	48.2	47.1	42.3	35.2	35.1	34	31.7	32.2	29.9	41.7	44.2	40.1
H_2	9.6	12.1	19.6	17.6	23.5	29	22	27.2	34	11.1	19.2	25
CO_2	21.9	18.4	16.2	29.6	22.8	20.3	27	23.7	21.7	27.1	17	16.2
CH_4	13.4	13.6	15.1	11.6	12.5	12.1	14.1	11.4	10.5	13.7	12.5	12.8
C_2-C_4	7	8.9	6.7	6.1	6.2	4.7	5.2	5.5	3.9	6.5	7	5.9
Mass balance (%)	95.4	93	98	89.6	91	89.5	103	93.8	99.9	95.8	102	99.1

Table 4.

Porous properties of the samples

Sample	BET (m^2/g)	Micropore volume (cm^3/g)	Mesopore volume (cm^3/g)
Tyre	71.7	0.090	0.561
Used Tyre char	63.8	0.080	0.468
RDF	85.3	0.068	0.126
Used RDF char	12.6	0.014	0.041
Date stones	5.2	0.006	0.004
Used Date stones	4.0	0.008	0.004

FIGURE CAPTIONS

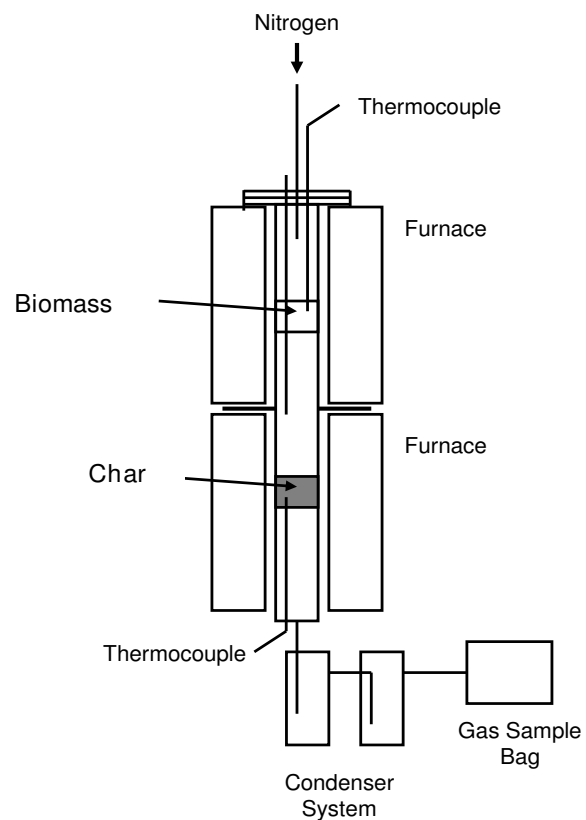Figure 1. 1(a) Schematic diagram of the waste pyrolysis reactor; 1(b) Schematic two-stage pyrolysis-gasification reaction system
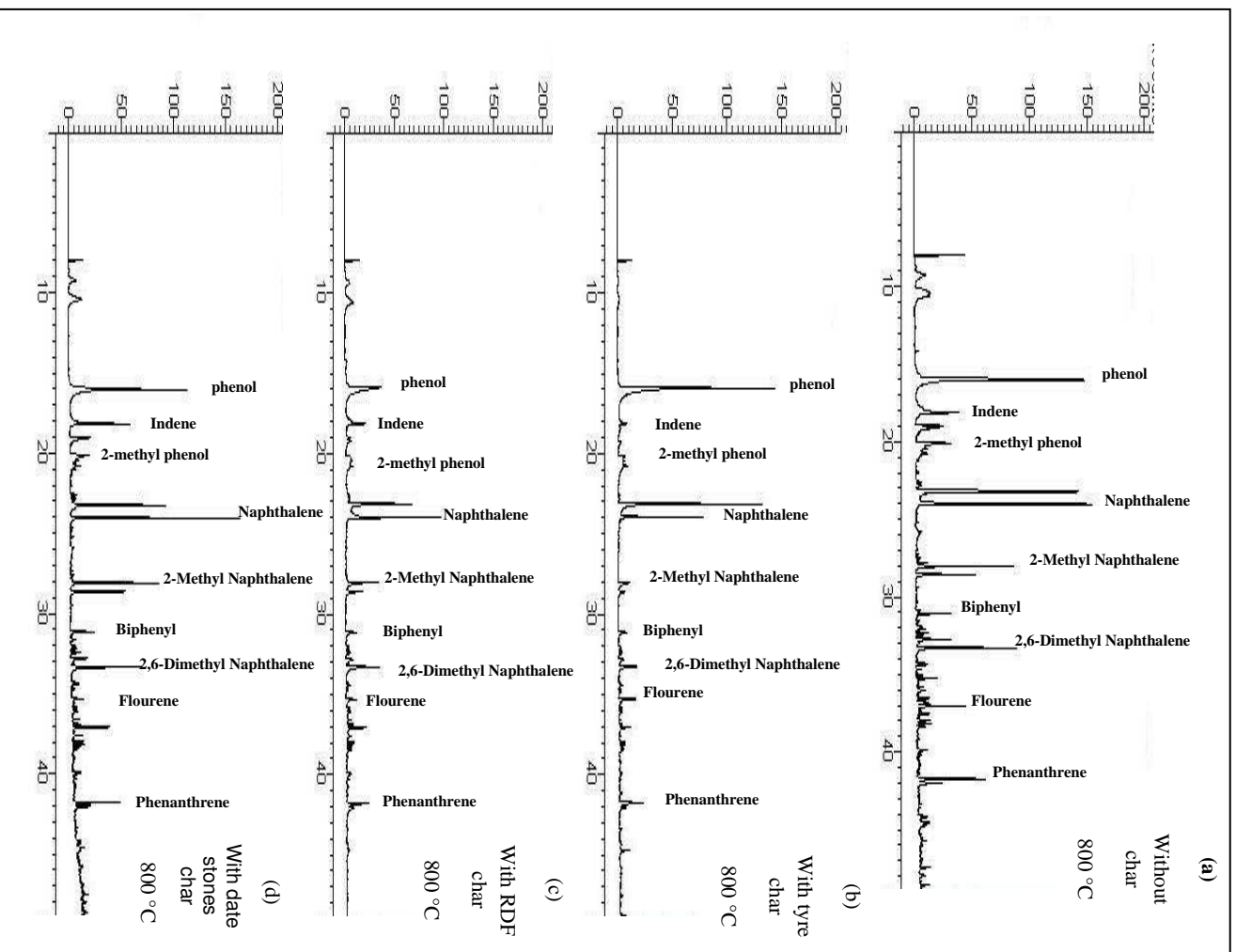
Figure 2. Effect of char type over tar composition at a cracking temperature of 800 °C
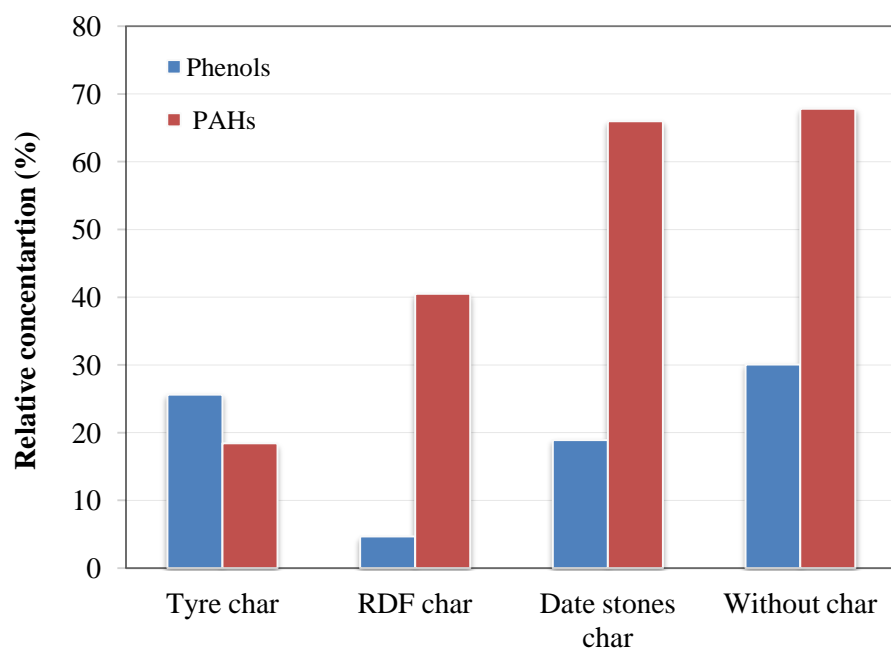
Figure 3. Tar composition with different carbon samples at a cracking temperature of 800 C.

Figure 4. Tar composition at different char cracking temperatures for (a) without char; (b) with tyre char

Figure 5. 5(a) Product yields and 5(b) gas composition in relation to biomass:char ratio for the tyre derived pyrolysis char at 700 °C hot char bed temperature.

(a)
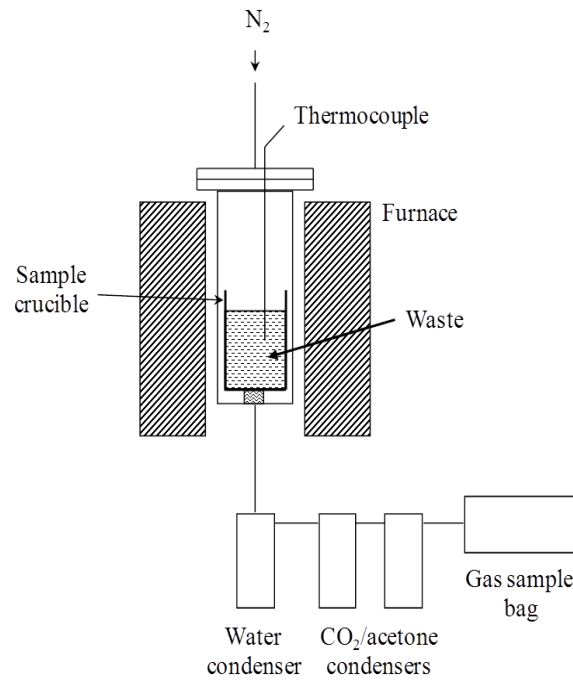
(b)

Figure 1. (a) Schematic diagram of the waste pyrolysis reactor (b); Schematic diagram of the two-stage pyrolysis-gasification reaction system

Figure 2. Effect of char type over tar composition at a cracking temperature of 800 °C

Figure 3. Tar composition with different carbon samples at a cracking temperature of 800 C.
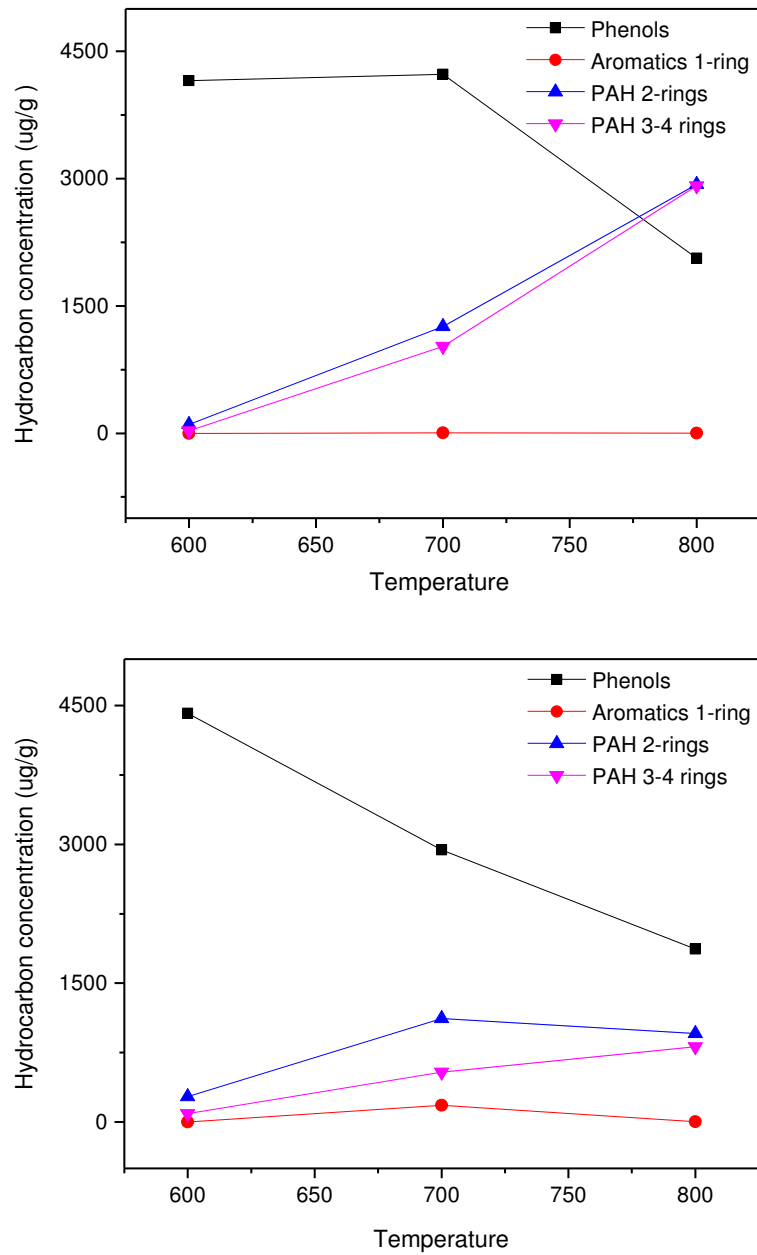
Figure 4. Tar composition at different char cracking temperatures for (a) without char; (b) with tyre char
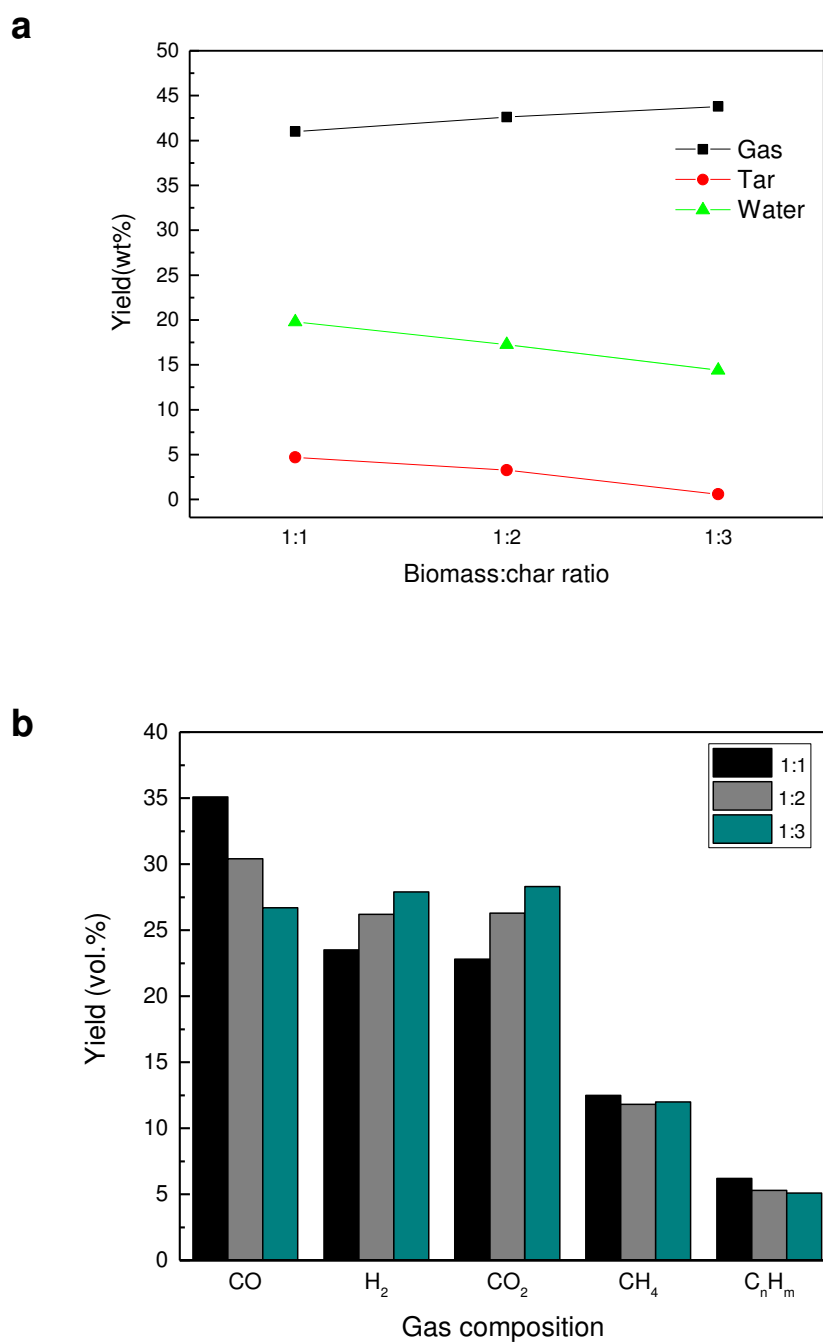
a

b

Figure 5.(a) Product yields and (b) gas composition in relation to biomass:char ratio for the tyre derived pyrolysis char at 700 °C hot char bed temperature.