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Hydrogen-rich syngas production and tar removal from biomass gasification using sacrificial tyre pyrolysis char

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Abstract

Carbonaceous materials have been proven to have a high catalytic activity for tar removal from the syngas produced from biomass gasification. The simultaneous reforming and gasification of pyrolysis gases and char could have a significant role in increasing the gas yield and decreasing the tar in the product syngas. This study investigates the use of tyre char as a catalyst for H_2-rich syngas production and tar reduction during the pyrolysis-reforming of biomass using a two stage fixed bed reactor. The biomass sample was pyrolysed under nitrogen at a pyrolysis temperature of 500 ºC, the evolved pyrolysis volatiles were passed to a second stage with steam and the gases were reformed in the presence of tyre char as catalyst. The influence of catalyst bed temperature, steam to biomass ratio, reaction time and tyre ash metals were investigated. The influence of the catalytic activity of tyre ash minerals on composition of syngas and tar decomposition during the steam reforming of biomass was significant as the removal of minerals led to a decrease in the H_2 yield. Raising the steam injection rate and reforming temperature resulted in an increase in H_2 production as steam reforming and char gasification reactions were enhanced. The maximum H_2 content in the product syngas of 56 vol.% was obtained at a reforming temperature of 900 °C and with a steam to biomass mass ratio of 6 (g g^{-1}). Further investigation of the influence of the biomass:steam ratio on syngas quality showed that the H_2:CO molar ratio was increased from 1.8 (steam: biomass ratio; 1.82 g g^{-1}) to 3 (steam: biomass ratio; 6 g g^{-1}).

Keywords; Waste tyre; Pyrolysis; Biomass gasification; Tar removal; Syngas

1. Introduction

Due to increasing concern in regard to environmental issues such as global warming and depletion of fossil fuels, hydrogen is considered as an important fuel of the future, which can reduce the reliance on oil. Hydrogen can be produced via various chemical processes including ion exchange membranes, biomass gasification, ethanol and methanol steam reforming. However, fossil fuel reforming, mainly natural gas, is known to contribute to about 90% of the current total hydrogen production [1, 2]. Therefore, there has been a growing effort to find alternative processes for hydrogen production. Gasification is one of the effective thermochemical conversion processes for biomass energy for producing a hydrogen rich gas which can be used for fuel cell systems and synthesis reactions including Fischer-Tropsch and methanol reactions [3]. Various gasifying agents are used during the gasification process depending on the desired gas composition [4]. Steam is well known to increase the heating value of syngas and produce a gas with a higher content of hydrogen [5]. However, tar formation during biomass gasification is one of the main problems which can prevent the direct use of the producer gas in gas turbines and gas engines. One of the most efficient techniques for tar removal is catalytic steam reforming in which tar compounds can be converted into useful gases and for this purpose various catalysts have been tested [4, 6-8]. To cope with the challenges associated with deactivation of commercial catalysts because of coking or sulphur poisoning, char as a by-product obtained in the pyrolysis of organic matter is cheap and easily replaceable and has been found to be effective for tar reforming during the volatile-char interactions [9-17].

Choi et al. [14] investigated the gasification of a sewage sludge with the use of activated carbon as a catalyst and reported that the introduction of steam at 800ºC enhanced the steam reforming reactions and produced a free tar syngas with a high content of hydrogen (35-45 vol.%). The authors concluded that with this process the total condensed liquid decreased from 20 to 14.4

wt.% and the product syngas increased from 52.5 to 64.9 wt.%. In contrast, Striugos et al. [16] claimed that the conversion of tar during the steam reforming of biomass was only 1% higher than that with no steam. It is well know that biomass has a high percent of moisture, therefore the auto-generated steam during the catalytic cracking could also act as a gasifying agent and enhance the cracking of tar compounds.

A comparison study of the catalytic activity of various additives including zeolite, olivine, dolomite and biomass and coal based activated carbons were investigated for tar removal and hydrogen production during air gasification of dried sewage sludge [18]. A large reduction in tar and the highest H_2 production (24.4 vol.%) were found with the use of coal based activated carbon as the tar removal catalyst. The authors attributed the higher activity of coal based activated carbon, among the catalysts used, to its high BET surface area and the large pore size. In another study carried out by Choi et al. [14], using original and acid-treated activated commercial carbons, with a BET surface area of 959 $m^2 g^{-1}$, were used as tar cracking additives during the steam/oxygen gasification of dried sewage sludge in a two stage gasifier. The acid treated activated carbon was found to be less effective than the original activated carbon, additionally the syngas obtained with the original activated carbon was found to have the highest H_2 content. It was suggested that the ash minerals present in the original activated carbon had an effective role in promoting tar cracking reactions and enhanced H_2 production during the steam reforming.

Tars are known to contain significant concentrations of polycyclic aromatic hydrocarbons (PAH) and according to the reported literature [19, 20], reforming of PAHs in the presence of steam at a temperature below 1000 ºC is very difficult. Therefore, there is a need to use catalysts with steam reforming to ensure cracking of the components of tar even at a temperature of 900 ºC. The tar decomposition using char is suggested to be due to multi steps including tar reforming on the char surface producing coke on char pores followed by steam gasification of the deposited carbon which means that tar reforming does not occur directly [21]. Regarding char gasification during the process of simultaneous reforming/gasification of pyrolysis oil and char, the volatiles formed during the pyrolysis process could be a strong inhibitor for char gasification [22, 23]. The carbon deposits or coke could be formed during the interaction of volatiles with the char surface. However, the presence of minerals could facilitate or enhance the char gasification as was observed by Bayarsaikhan et al. [22]. They investigated the steam gasification of the acid-washed char and found that the net char conversion was negative, which suggests that the coke deposits on char surface without being gasified or the tar deposition rate is faster than the steam gasification rate.

There has been growing interest in converting wastes into useful products. The pyrolysis of waste tyres produces an oil, char and gas product in addition to the steel reinforcement [24]. The oil yield is high (up to ~58 wt.%) from the tyre rubber and has fuel properties similar to a light fuel oil and consequently can be used as a valuable liquid fuel. The yield of gas is about 10 wt.% which has a high concentration of hydrocarbon gases with a calorific value in the range of 20─65 MJ m^{3}, depending on process conditions and therefore can be used as process fuel for the pyrolysis system. The char yield is ~35─40 wt.%, and may be used as a solid fuel or low grade carbon black because of the rather high ash content. However, tyre char produced during the pyrolysis of waste tyre has been found to have a high catalytic activity for tar cracking from biomass gasification [25]. The presence of tar in the syngas produced from biomass and wastes is a complex mixture of condensable hydrocarbons and has been shown to be problematic in that it causes blockage of process lines, plugging and corrosion in downstream fuel lines, filters, engine nozzles and turbines.

In this study, tyre char is used for tar reforming and hydrogen production through a gas-solid simultaneous reforming/gasification process using a two stage pyrolysis-reforming reactor which could play a major role in increasing the total gas yield. The study investigates the influence of bed temperature, steam to biomass ratio, reaction time and the effects of tyre ash minerals on syngas quality and hydrogen production. Biomass in the form of wood pellets produced from waste wood was used as the feedstock to generate tar/syngas and waste tyre derived pyrolysis char was used as a sacrificial catalyst in a steam reforming process to generate a hydrogen-rich syngas.

2. Materials and methods

2.1 Materials

Wood pellets with a particle size of 1 mm were used as the biomass feedstock for pyrolysis reforming/steam gasification experiments. The wood pellets were produced as compressed saw dust pellets from waste wood processing by Liverpool Wood Pellets Ltd, Liverpool, UK. Tyre pyrolysis derived char was used as a catalyst for reforming of biomass pyrolysis volatiles and was prepared using a fixed bed reactor. Details of the production of the tyre char are reported elsewhere [25], but briefly the pyrolysis reactor was constructed of stainless steel, externally heated by an electrical furnace and the waste tyre was heated in nitrogen at a heating rate of 10 ºC min^{-1} to a final temperature of 800 ºC and held at that temperature for one hour. The recovered pyrolysis chars were ground and sieved to a particle size of ~1mm and oven-dried for 24h.

To study the catalytic effect of ash minerals on biomass tar reforming, tyre char was demineralised using HCl to reduce its ash content. For this purpose, (5M) HCl was added to tyre char followed by boiling the mixture for 20 minutes. Then, the char was washed several times with deionised water until the pH was 7, finally the demineralised tyre char was dried at 105°C for 24h. The elemental composition and ash content of the char samples are shown in Table 1. Tyre char had a high ash content of 18 wt.% and its main metal composition was Zn and the acid treatment was effective for metal removal. After the removal of metals, the carbon content of acid treated char increased while the sulphur and nitrogen contents decreased.

2.2 Pyrolysis and reforming reaction system

The experimental system consisted of a two stage pyrolysis-reforming reactor (Figure 1) constructed of stainless steel with an inner diameter of 22 mm and of a total length of 160 mm. The pyrolysis of biomass was carried out in the first stage at a temperature of 500 °C, and the evolved pyrolysis gases were passed directly to the second stage where steam catalytic reforming took place with the presence of tyre char. Each of the reactor stages were heated separately using temperature controlled and monitored furnaces. In addition, the biomass sample temperature and the tyre char temperature were monitored separately. Temperature monitoring throughout was via type K thermocouples. The first stage and second stage reactor system was continually purged with nitrogen at a metered flow rate of 90 ml min^{-1}. The reforming temperature was varied between 700 and 900 °C. The experimental procedure consisted of initial heating of the second stage hot char reactor to the desired catalyst temperature and once the desired temperature was reached, the biomass sample was then pyrolysed at a heating rate of 40 °C min^{-1} from ambient temperature to a final temperature of 500 °C. At the same time, water was injected via a syringe pump at the feeding rate of 6.64 g h^{-1} (steam/biomass (S/B) ratio of 3.32) into the second stage of the reactor, and mixed with the evolved pyrolysis gas and passed over the tyre char. Further experiments were carried out to investigate the influence of steam to biomass ratio on the gaseous composition and hydrogen production at S/B ratios of 1.82, 3.32, 4.32 and 6g g^{-1}. Downstream from the reactor, the produced gas was passed through two cold traps (-70 °C),where tar compounds and also unreacted water were condensed. The non-condensable gases were collected using a Tedler™ 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 influence of the experimental conditions on the gas composition and reforming/gasification process was investigated. The experimental parameters used in this study were, bed temperature (700-900 °C), S/B mass ratio (1.82 ─ 6.00) and reaction time (1-4h).

2.3 Products analysis

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 a80-100 mesh HayeSep column. A separate Varian CP-3380 gas chromatograph fitted with a 60-80 mesh column and a flame ionization detector (FID) was used to analyse the hydrocarbons (C_1-C_4) using nitrogen as carrier gas with a HayeSep GC column.

The condensed liquid was analysed using coupled gas chromatography-mass spectrometry (GC-MS). Prior to analysis the product bio-oil/tar was passed through a sodium sulphate column (Na_2SO_4) to remove any residual water. The GC-MS used was a Varian CP-3800 gas chromatograph coupled with a Varian Saturn 2200 GC- mass spectrometer. An aliquot (2 µl) of the bio-oil/tar dissolved in dichloromethane solvent was injected into the GC injector port at a temperature of 290 °C; the oven programme temperature was 40 °C for 2 min, then ramped to 280 °C at a heating rate of 5 °C min^{-1}, and finally held at 280 °C for 10 min. The transfer temperature line was 280 °C, manifold at 120 °C and the ion trap temperature was held at 200 °C.

The ash content of char samples was analysed using thermogravimetric analysis (TGA) under an air atmosphere. Elemental analysis was carried out with a CE Instruments Flash EA2000. The tyre char minerals of both original and acid treated tyre char were determined by EDX. Fresh and selected reacted char samples were analysed using a Stanton-Redcroft thermogravimetric analyser (TGA) for carbon deposition. About 15 mg of char sample was placed in an alumina sample pan and heated at a heating rate of 20 to 800 °C and held for 20 min under the atmosphere of air at a flow rate of 50 ml.

3. Results and discussion

3.1 Effects of char ash on tar decomposition

To examine the influence of ash minerals on tar cracking and increasing the hydrogen yield during biomass pyrolysis-reforming/gasification process, tyre char was subjected to acid treatment with HCl for the purpose to remove the minerals. As observed in Table 1, the treatment was effective in removing about 50% of the total ash content of the char, including removal of most of the zinc, calcium and iron. It has been reported [26] that the ash content of a typical tyre is between 5 and 7 wt.% depending on the type of tyre, comprising mainly additives such as silica and clays, in addition to the additives such as zinc and sulphur. The silica and clay (alumina-silicates) additives would not be removed by the acid treatment process and would account for the large majority of the 9 wt.% ash content of the demineralised tyre char. It might be expected that the acid treatment process would remove most of the reactive metal from the tyre char, leaving the silica and alumina-silicate filler material. The porous texture of the treated sample remained unaffected. The original and acid-treated tyre chars were used as catalysts for tar cracking during biomass reforming in the presence of steam. With both chars, the influence of bed temperature on the final gaseous compositions was investigated from 700 to 900 °C, at a steam to biomass mass ratio of 3.32 and a reaction time of 60 min. The final temperature of the pyrolysis of the biomass was always 500 °C.

The reforming and cracking of biomass volatile compounds and the gasification of tyre char produce more gaseous products according to the following reactions [27, 28];

Water gas (primary)	$C + H_2O \leftrightarrow CO + H_2$	Eq.1
Water gas (secondary)	$C + 2H_2O \leftrightarrow CO_2 + 2H_2$	Eq.2
Boudouard	$C + CO_2 \leftrightarrow 2CO$	Eq.3
Methanation	$C + 2H_2 \leftrightarrow CH_4$	Eq.4
Water gas shift	$CO + H_2O \leftrightarrow CO_2 + H_2$	Eq.5
Steam reforming	$C_nH_m + nH_2O \leftrightarrow nCO + \left(n + \frac{m}{2}\right) H_2$	Eq.6
Methane steam reforming	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	Eq.7

As can be observed from the experimental results presented in Table 2, with both tyre char samples, total gas yield increased significantly with the increase of temperature to 900 °C, this is due to the reforming of tars (Eq.6) and the char gasification, as in the second stage the reactions of H_2O, CO, H_2 and CO_2 with carbon in the tyre char took place [5]. With the use of original tyre char, the gas yield, hydrogen yield and HHV of the product gas increased from 52.8 to 131.6 (wt.%), 8.4 to 39.2 (mmol g^{-1} biomass) and 48.3 to 66.1 (MJ Kg^{-1}) respectively as the tyre char temperature was increased from 700 to 900 °C. According to Franco et al. [29], the endothermic char gasification reactions are enhanced at a higher temperature which can be clearly seen from the decrease of tyre char recovered after reaction at higher reaction temperature (Table 2). It is worth mentioning that in the experiment with the use of sand and steam at 900 °C, the total gas yield decreased by 56%, while the liquid product increased by 27%. Therefore, the increase of gas yield at a higher reforming temperature with the presence of tyre char is mainly due to the catalytic properties of char for reforming of tar and also because of char gasification.

The catalytic effect of the acid treated demineralised tyre char was investigated using the same experimental conditions as with the original tyre char. As presented in Table 2, the acid treated char exhibited a lower catalytic activity than the original tyre char. For example at a temperature of 900 °C, the total gas yield decreased by ~20% with the acid treated tyre char compared to the original gas yield at 900 °C. Additionally, the total liquid product was found to be higher with the acid treated tyre char. The results suggest that the ash metals, present in tyre char, play a significant role in enhancing the tar reforming reactions during the biomass pyrolysis-reforming/gasification process.

As displayed in Figure 2, the tyre char temperature had a clear influence on the gaseous species found in the product syngas. The main gaseous compounds formed during this process was hydrogen. The hydrogen yield increased with temperature, the maximum hydrogen yield of 39.20 (mmol g^{-1}) was obtained at a temperature of 900 °C. However, the removal of minerals as a result of acid treatment, resulted in a decrease in the hydrogen yield to 30 mmol g^{-1}. The decrease in hydrogen yield with the use of acid treated tyre char was also observed at reaction temperatures of 700 and 800 °C. Ma et al. [30] obtained a hydrogen yield of 83.3 mol kg^{-1} from the steam gasification of bio char.

With regards to the gaseous composition formed with the use of original and acid treated tyre char, there is an obvious difference between the two types of tyre pyrolysis char, e.g. the hydrogen and CO_2 content were higher with the original tyre char. For example at a temperature of 700 °C, the hydrogen content decreased from 34.6 to 14.3 vol.% after the acid treatment of the tyre char. Additionally, the content of CO, CH_4, C_nH_m increased with the use of acid treated tyre char. This suggest that steam reforming of methane and water gas shift reactions were enhanced greatly with the presence of metals in the tyre char. The same observation has been found by Zhang et al. [31].

Table 2 shows that the H_2/CO molar ratio decreased sharply with the removal of minerals from the tyre pyrolysis char. The results suggest that the ash metals present in the tyre char promote the water gas shift reaction (Eq.5) and the char-steam reactions (Eq.1 & Eq.2). The increase of H_2 concentrations with the original tyre char is mainly attributed to the catalytic effect of mineral metals which play a major role in enhancing the catalytic steam reforming and cracking of tar. Additionally a significant difference was also observed in relation to the hydrocarbon concentration of the product gas with both chars. The same trend was observed by Jiang et al. [32], during the steam gasification of rice straw, in which the hydrogen yield was found to decrease from 10 mmol g^{-1} of the original sample to 8.8 mmol g^{-1} of acid treated sample. According to Choi et al. [14], the adsorbed tar on the active sites of activated carbon could form coke and with the sequence of thermal and catalytic cracking of tar and coke, hydrogen and light hydrocarbons are produced. The active sites could be the metals, therefore the available active sites on the acid treated tyre char were reduced.

In comparison with the experiments carried out with the use of sand in the second stage catalytic reactor at 900 °C, the concentration of CO decreased with the use of tyre pyrolysis char during the steam reforming of biomass pyrolysis oil, this indicates that the char promotes the CO-shift reaction leading to a high concentration of H_2 and CO_2 [27]. Similar results have been reported by Wang et al. [33]. A significant decrease in methane concentration was observed as well. The detected trend in this study agrees with the trend observed by Franco et al. [29]. The influence of gas-char interaction on gaseous composition has been studied by Chen et al. [34] and concluded that this process had a significant influence on enhancing the hydrogen content from 17 to 37.8 vol.%. According to the reported literature, the water gas shift reaction is promoted at a temperature higher than 700 °C leading to an increase in H_2 and decrease in CO yields [29].

Tyre char promotes the water gas shift reaction at higher temperature leading to a high concentration of H_2. However, the increase in CO_2 composition is not significant. According to Franco et al. [29], other reactions may take place at a temperature higher than 830 °C such as Boudouard reaction which results in consuming the CO_2 concentration and this can be observed from the amount of converted tyre char at 900°C which was higher than that at 800 °C. Additionally, char steam gasification reactions and methane reforming reaction are enhanced at 900 °C, resulting in an increase in CO content and a decrease in the CH_4 content. The significant increase in H_2 concentration is also due to hydrocarbon cracking and reforming reactions. Wang et al. [9] studied the steam reforming of biomass and found that the steam itself had a minor effect on tar reforming without the presence of char-supported catalyst.

The presented results suggested that tyre ash metal species had a catalytic role in enhancing the hydrogen production. Zhang et al. [31] studied the catalytic conversion of model biomass pyrolytic vapour using biochar and demineralised biochar and reported hydrogen yields of 64 and 59 vol.% respectively. Nanou et al. [35] investigated the influence of ash on enhancing the steam gasification of wood char and concluded that the addition of ash minerals to the biomass char was effective in enhancing the char gasification as the gasification rate of the impregnated char increased by 30% compared to the original char with no minerals. In this study, this can be observed from the decrease in tyre char recovered at the end of the experiment. At all the studied temperatures, the decrease in the original tyre char recovered was more obvious than the acid treated char (Table 2). This could be due to the presence of metals which could enhance the char gasification. For example at 900 °C, the original and acid treated tyre char yields decreased by 17.5 and 14.5 % respectively.

The catalytic effect of zinc in enhancing the hydrogen yield during biomass gasification has been reported before by other researchers [1]. Gonzalez [1] examined the influence of the presence of $ZnCl_2$ and dolomite on biomass steam gasification and concluded that at a temperature of 800 °C, the presence of $ZnCl_2$ had a positive effect in promoting the hydrogen production, compared to dolomite, during biomass gasification in the presence of steam. However, at a temperature of 900 °C, the hydrogen concentration remained almost the same even in the presence of $ZnCl_2$. Demirbas [36] compared the catalytic pyrolysis of biomass samples with Na_2CO_3, K_2CO_3 and $ZnCl_2$ and the highest hydrogen yield of 70.3% was obtained from olive husk using 13% $ZnCl_2$ as catalyst at 1025 K. In contrast, Hamad et al. [37] claimed that $ZnCl_2$ had a negative influence in which the gas yield was found to decrease with the addition of $ZnCl_2$ to biomass.

The tar compounds found in the condensed liquid were grouped based on the classification system reported by other researchers in which the tar compounds are classified into five classes depending on the number of aromatic rings and the molecular weight [38, 39]. Class 2 includes tar compounds with heterocyclic compouds such as phenols and cresols, Class 3 is referred to as aromatic tar compounds with 1-ring such as ethylbenzene and xylene, Class 4 contains 2-3 ring aromatic compounds such as naphthalene, methylnaphthalenes and phenanthrene and Class 5 tar compounds contain 4-7 ring aromatic compounds such as fluoranthene and pyrene.

The concentration of the classified tar compounds is shown in Figure 3, for the product tars produced using both the original tyre char and the acid-treated tyre char shows that the major tar compounds present came from class 2. The presence of minerals in tyre char seems to promote the cracking of large ring polyaromatic compounds (class 4 & 5) to form light compounds (class 2). Additionally, it can be observed that the concentration of both the light and heavy PAH compounds were increased by 10 and 2 % respectively with the use of acid treated tyre char. In terms of the catalytic activity of the char used in this study, the results show that the original tyre char was more effective in reducing most of the tar compounds than the acid-treated tyre char. Jiang et al. [32] studied the catalytic effects of the inherent alkali and alkaline earth metals on tar decomposition during the steam gasification of biomass via using original biomass and demineralised biomass and reported that the inherent alkali minerals present in biomass char had a significant catalytic effect in enhancing tar reforming, char gasification and water gas shift reactions during the biomass steam gasification [32]. However, char ash consists of various metal species and the catalytic activity of the metals may not be the same, therefore, Zhang et al. [31] carried out another study to investigate the catalytic effects of specific metals on biomass pyrolysis tar cracking, for this purpose biochar was impregnated with different metallic species (K, Ca, Mg, Zn, Fe, Al). It was reported that all the studied metallic elements had a catalytic activity except for Al. The presence of zinc in the tyre ash composition plays a significant catalytic role in enhancing tar reforming reactions. For example, in the study by Altuntaş Öztaş and Yürüm [40] coal samples were impregnated with several metals including Zn. The authors observed some catalytic effect of Zn and Ni in decomposing many of the tar compounds.

3.2 Effect of Steam to biomass ratio

The main aim of the combination of biomass pyrolysis and tar and char gasification in the second stage was to enhance the gas yield and obtain the optimum syngas ratio through shifting the reaction from exothermic to endothermic [41, 42]. Therefore, the influence of steam to biomass (S/B) mass ratio over the range of 1.8-6.0 on hydrogen production and reforming/gasification efficiency was investigated at 900 °C and at reaction time of 60 min with the use of the original tyre char. According to the reported literature [33, 43], the metal species in char accelerates the dissociation of water into OH* and O* intermediates which would then react with the cracked molecular hydrocarbons intermediates, formed during the reforming process, thus promoting the water gas shift reaction and generate hydrogen. Therefore, this process depends on the amount of the dissociated species from water (H* and OH*). The hydrogen production yield could be increased by varying the steam to biomass ratio.

The influence of steam to biomass mass ratio on the total gas yield and gas compositions is shown in Figure 4. The increase in steam quantity enhanced the steam reforming of tar and tyre pyrolysis char-steam reactions which results in an increase in the gas yield from 94.82 to 132.6 wt.% (data calculated in relation to the original mass of biomass). The total gas yield increased by ~28% with the increase of steam flow rate (S/B ratio 1.82 to 3.32). At higher S/B mass ratio of 3.32, the effect of steam on gas production was negligible. According to Alipour et al. [44], the high steam to biomass ratio does not always contribute to increase the total gas yield.

As the steam to biomass ratio was increased from 1.8 to 6.0, the hydrogen concentration increased from 47 to 56 vol.% and the CO concentration decreased from 26 vol.% to 19 vol.%. The increase of H_2 and decrease in CO at higher S/B mass ratio is due to the enhanced char steam gasification (Eq.1) and water gas shift reaction (Eq.5). However, the increase of H_2 concentration was not significant when the S/B mass ratio was higher than 3.32. In a study undertaken by Zhang et al. [31], the highest hydrogen yield achieved, during the reforming of bio oil using bio char, was about 60 vol.% at a steam to model pyrolytic vapour ratio of 4 and a reaction time of 30 min.

Sattar et al. [45] investigated the influence of steam flow rate on the product gases during the gasification of bio-chars and reported an increase in the hydrogen and CO_2 yields with increasing steam flow rate. However in this study both CO and CO_2 yields decreased with an increase in the steam flow rate which could be due to multiple reactions occurring at the same time, such as water gas shift, reforming and char gasification. Yan et al. [28] studied the influence of steam on the gasification of biomass char at a temperature of 850°C and reported an increase of H_2 yield from about 2.15 mol kg^{-1} to 57.07 mol kg^{-1} with the increase of steam input from 0 to 0.165 g min^{-1} g^{-1} of biomass char.

As observed in Figure 5, with the increase of S/B mass ratio, the H_2/CO molar ratio increased while CO/CO_2 decreased which suggests that the water gas shift reaction determines greatly the H_2production. The same trend was observed by Wei et al. [46]. The H_2/CO ratio is important in determining the end use of the syngas. The optimum value of H_2/CO is determined by the required application, for example the upgrading of syngas for fuel cell applications require a higher H_2/CO while a value of 2:1 is needed for Fisher-Tropsch reactions [47]. It is reported that it is costly to produce synthesis gas with a H_2/CO molar ratio of between 1 ─ 2 [48]. In this study, the experiments performed at a steam/biomass ratio of 3.3 and 4.3 produced a syngas ratio of 2 which is more suitable to be used for Fisher-Tropsch synthesis. The HHV increased in the range of the studied S/B ratio to 72 MJ/Kg. Based on the hydrogen concentration and total gas yield, it can be concluded that that the optimum steam to biomass ratio for this system is 3.32. Zhang et al. [31] studied the influence of steam on model pyrolytic vapour (2-5 g/g) on the gaseous composition using biochar and concluded that the ratio of 4 was the optimum.

With regards to the tyre char gasification and S/B ratio, the steam enhanced the char conversion as the residual material (reacted tyre char) recovered after the gasification was found to decrease with increasing steam to biomass ratio. The higher S/B mass ratio enhanced the tyre char gasification as the amount of tyre pyrolysis char recovered after reaction was found to decrease from 90% at a S/B ratio of 1.8 to 73.5 at a S/B ratio of 6.0. Therefore the increase of gas yield at a higher S/B ratio was also due to char gasification as has been mentioned before. High steam to carbon ratio is required to avoid coke accumulation on the surface of the tyre char [49]. However, the decrease was not significant, the increase of steam flow rate by about 70% led to a 20 % decrease in the amount of final tyre char recovered. Chen et al. [34] reported a 6 % decrease in char yield when the S/B ratio was increased from 1 to 4. The char conversion rate can be better enhanced with a long reaction time.

3.3 Effect of reaction time

Further experiments were carried out to investigate the influence of reaction time on tyre char gasification at a temperature of 900 °C, to determine whether the char conversion and total gas production could be enhanced by allowing the reaction to proceed for several hours. The variation in gas compositions with reaction time is shown in Figure 6. With the increase in reaction time the H_2 concentration remained almost constant and the CO concentration increased. Chaudhari et al. [47], reported that the hydrogen concentration was found also to remain constant after 1 h reaction time.

The increase of hydrogen formation during the biomass gasification is mainly due to the reactions of tars and hydrocarbons with char. As can be observed from the gaseous compositions presented in Figure 6, the hydrogen content remained almost constant with the increase of reaction time from 1h to 2h and only a slight increase was observed at a reaction time of 4h. Additionally, the CO/CO_2 molar ratio increased with time on-stream, while H_2/CO decreased. These results suggest that the reaction time is complete in 60 min and Boudourad (Eq.3) and char reactions with steam (Eq.1) are the dominant reactions after 60 min. This agrees with the evolution of CO/CO_2 and H_2/CO with time. The high H_2/CO at a reaction time of 60 min is due to the influence of water gas reactions and over the reaction time of 60 min, the char reactions with CO_2 and steam are more important which could explain the increase in CO/CO_2 ratio. However, a decrease in the ratio of CO/CO_2 was observed with the increase in reaction time from 2 h to 4 h, this is due to the gasification of the total fixed carbon so there was no carbon left in tyre char to react with steam and as a result CO/CO_2decreased.

The increase of gas yield with time was found to be correlated with the increase of carbon conversion of tyre char as displayed in Figure 7. The char conversion was calculated from;

$$C_o - C / C_o$$

Where C_o = carbon mass of tyre char before reaction and C = carbon mass after reaction

For example, the tyre char carbon conversion increased by 50% with the increase in reaction time from 1 h to 2 h and the same percentage of increase was observed in the total gas yield which suggests that the increase in gas yield with time is mainly due to char gasification. For example, the carbon conversion of tyre char increased from 5 to 56% with an increase in reaction time form 1 h to 2 h. Accordingly, the total gas yield increased from 131.55 to 183.40 wt.% (in relation to the original mass of biomass).

As the main aim of this study was to increase the total gas yield through tar reforming and char gasification, the results displayed in Figure 7 shows that the reaction time had a significant influence on decreasing the amount of tyre char recovered after reaction. With a reaction time of 4 h, the final tyre char recovered was 6 wt.%, which included carbon and ash, and from figure 8, the carbon and ash represent 19.3 and 85 wt.% respectively. The carbon content decreased significantly from 80.6 wt.% after one hour to 19.3 wt.% after 4 hours (Figure 8). A complete conversion of tyre char was almost achieved with 4 h reaction time. This is agrees very well with the results presented in Figure 6.

As tyre char is expected to be gasified with the presence of steam at high gasification temperature, blank experiments of tyre char and steam was carried out where tyre char was gasified at 900 C for 1 hour (in the absence of biomass in the first pyrolysis stage) with the same experimental conditions as for biomass steam reforming over tyre char. The total gas yield produced from the gasification of tyre char itself was 35.49 wt.% compared to 131.6 wt.% (Figure 7) obtained with biomass tar reforming over tyre char. Therefore, tyre char gasification contributed to about 26% of the total gas yield obtained with biomass tar reforming experiments. Further experiments at 1.5h, 2h and 4 h showed that the total gas yield from the steam gasification of the tar char (in the absence of biomass) was 55.13 wt.%, 80.36 wt.% and 152.14 wt.% respectively. By comparison with the data in Figure 7, at 1.5 h the contribution of the tyre char gasification to the total gas yield was 35.5%, after 2 h it was 43.8% and after 4 h the total gas yield contributed by the tyre char gasification was 78.9% of the total gas yield.

In this work, char derived from the pyrolysis of waste tyres has been shown to be effective for the cracking and degradation of gasification tar-like compounds during the pyrolysis-catalytic steam reforming of biomass. The metallic mineral content of the tyre pyrolysis chars making a significant contribution to the tar degradation. In addition, the char reacts with the steam to generate hydrogen, and also carbon monoxide, and methane which add to the calorific value of the product syngas. Through the reactions of the tyre char with the steam, the char catalyst for reforming/gasification reactions is consumed or 'sacrificed' as a catalyst. An overall process concept could be, pyrolysis of waste tyres to recover, valuable tyre pyrolysis oils which have similar properties to a petroleum derived light fuel oil, recovery of steel from the pyrolysis char for recycling into the steel industry, and a product gas with high calorific value that can be used as process fuel for the tyre pyrolysis process [24]. The product char from tyre pyrolysis may then be used as a catalyst for the cracking/reforming/gasification of tars from the gasification of biomass to produce as clean syngas, whilst also contributing to the yield of the biomass syngas through tyre char gasification reactions.

4. Conclusions

In this paper, biomass pyrolysis gas and char gasification was investigated to produce hydrogen. The thermal cracking of biomass pyrolysis gases with the presence of steam at a temperature of 900 °C had a small influence on hydrogen production as only 10.94 mmolg^{-1}of hydrogen was obtained for the pyrolysis-reforming of biomass with sand. The hydrogen production increased significantly with the use of tyre pyrolysis char in the 2nd stage reforming/gasification reactor to be 39.20 mmol g^{-1} biomass due to the simultaneous reactions of tar reforming and char gasification. On the other hand, acid treated tyre pyrolysis char exhibited a lower catalytic activity as the hydrogen production decreased to 30.4 mmol g^{-1} biomass at 900 °C. The difference in hydrogen production between the original and acid-treated tyre char suggests that the metals in tyre char have a significant catalytic effect in enhancing the water gas shift, tar reforming and char-steam reactions.

The influence of operating conditions including catalytic reforming temperature, steam/biomass (S/B) mass ratio and reaction time were investigated for the purpose of obtaining a high hydrogen production. Among the studied variables, the reforming temperature had the greatest influence on hydrogen production. The results showed that the gas yields and hydrogen production increased with the increase of reforming temperature and S/B ratio due to the enhanced char steam gasification and water gas shift reactions.

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Table 1.

Ultimate and mineral content of char

	Original tyre char	Acid treated tyre char
Ash (wt.%)	18.9	9
Ultimate analysis (wt.%)		
Carbon	70.06	86.04
Hydrogen	0.28	0.33
Nitrogen	0.83	0.37
Oxygen (by difference)	4.78	0.73
Ash composition (wt.%)		
Zn	6.5	ND
K	0.05	0.05
Ca	0.95	ND
Fe	0.69	0.08

Table 2.

Influence of char minerals on product distribution and gas characterization

	Tyre char			Acid treated tyre char		
Temperature (°C)	700	800	900	700	800	900
Mass balance based on the biomass sample + water (wt.%)						
Gas	12.1	16.6	33.0	11.6	15.8	26.1
Liquid	82.8	76.87	61.4	84.5	79.9	69.5
Biomass char	5.6	5.8	5.5	5.5	5.9	5.5
Mass Balance	100.5	99.2	99.8	101.6	101.0	97.5
Tyre char recovered (%)	100	91	82.5	101	98	85.5
Mass balance based on the biomass sample (wt.%)						
Gas	50.0	66.7	131.6	48.9	63.1	106.8
Biomass char	23.0	23.3	22.0	22.5	23.5	22.5
Gas characterization						
HHV (MJ/Kg)	48.3	52.5	66.1	27.9	44.3	63.6
H_2 yield (mmol/g)	8.4	12.5	39.2	2.7	8.6	30.5
H_2+CO (mol/mol)	14.8	21.7	57.8	10.2	20.0	52.0
H_2/CO (mol/mol)	1.31	1.37	2.11	0.37	0.75	1.41

FIGURE CAPTIONS

Fig. 1. Schematic diagram of the two-stage pyrolysis-reforming/gasification reaction system

Fig. 2. Gas compositions and hydrogen yield with original and acid treated tyre chars

Fig. 3. Concentration of the classified tar compounds in the tar collected from the pyrolysis-reforming/gasification of biomass with tyre char catalyst at 800 °C (Class 2 = heterocyclic compouds e.g. phenols and cresols; Class 3 = 1-ring aromatic compounds e.g. ethylbenzene and xylene; Class 4 = 2-3 ring aromatic compounds e.g. naphthalene and phenanthrene; Class 5 = 4-7 ring aromatic compounds e.g. fluoranthene and pyrene.

Fig. 4. The influence of steam to biomass (S/B) ratio on gas composition and total gas yield

Fig. 5. Effect of steam to biomass ratio on H_2yield, HHV, H_2/CO and CO/CO_2.

Fig. 6. The influence of reaction time on the product gas compositions and H_2/CO and CO/CO_2 ratios in the syngas

Fig. 7. The influence of reaction time on tyre char conversion and total gas yield

Fig. 8. Carbon and ash content of tyre char from catalytic gasification of biomass at different reaction times

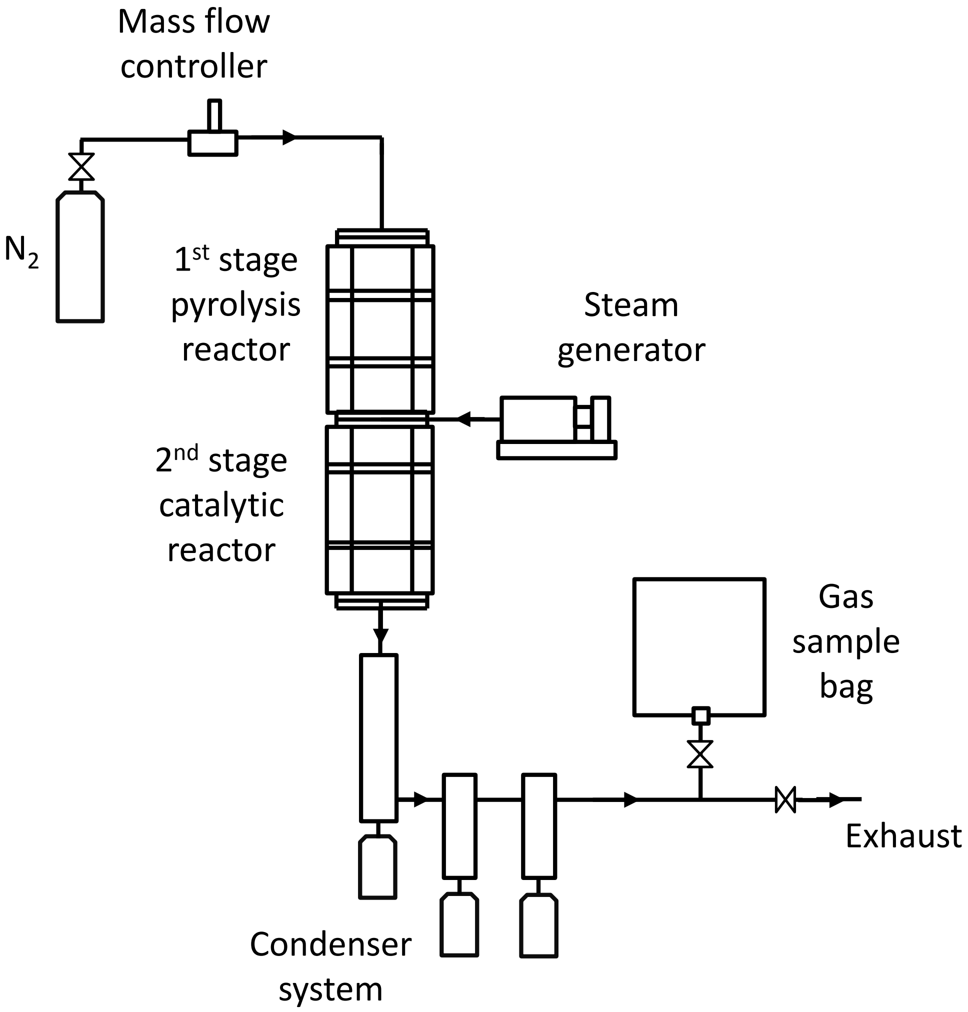


Fig. 1. Schematic diagram of the two-stage pyrolysis-reforming/gasification reaction system

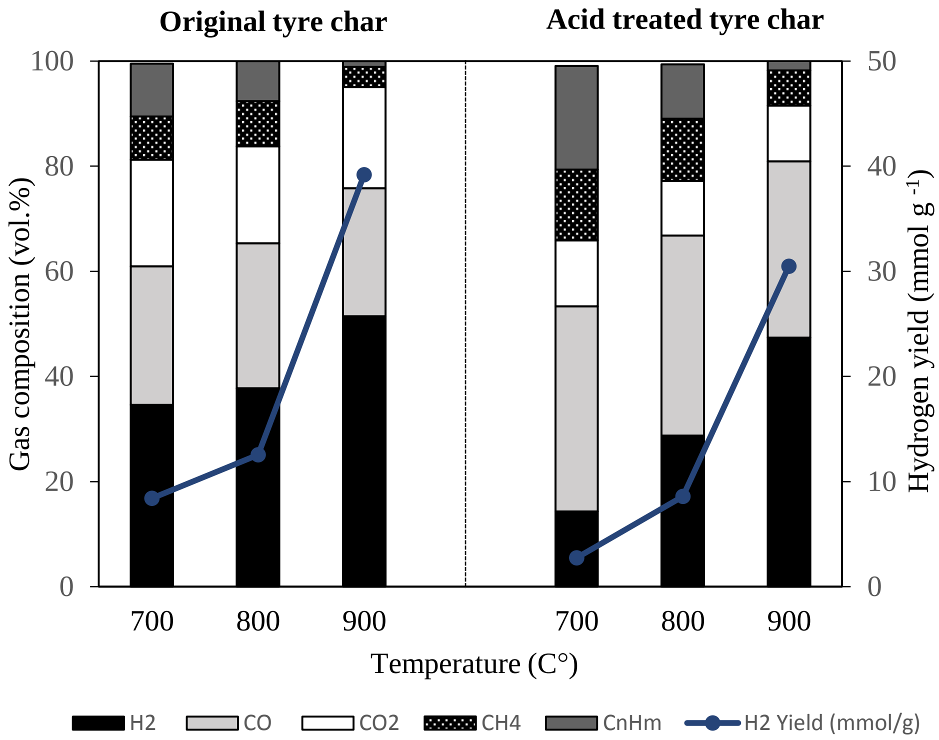
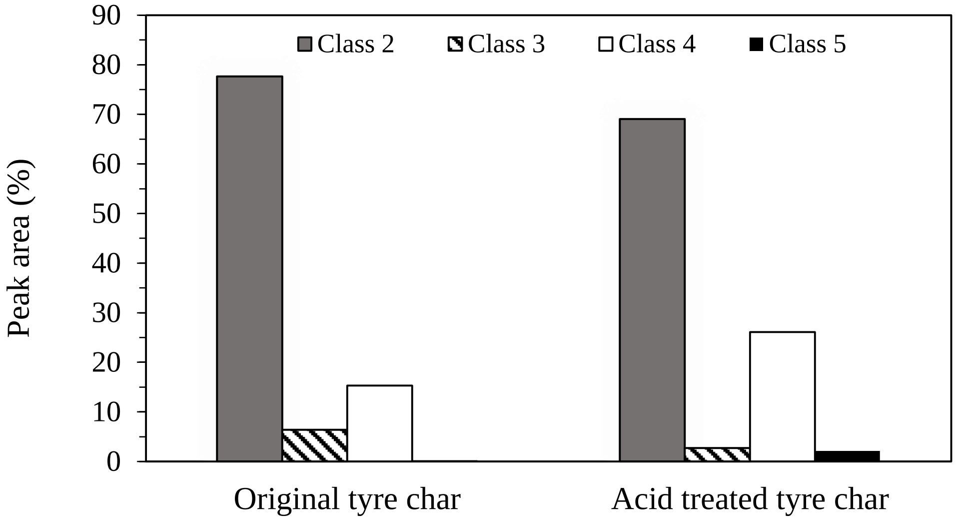


Fig. 2. Gas compositions and hydrogen yield with original and acid treated tyre chars



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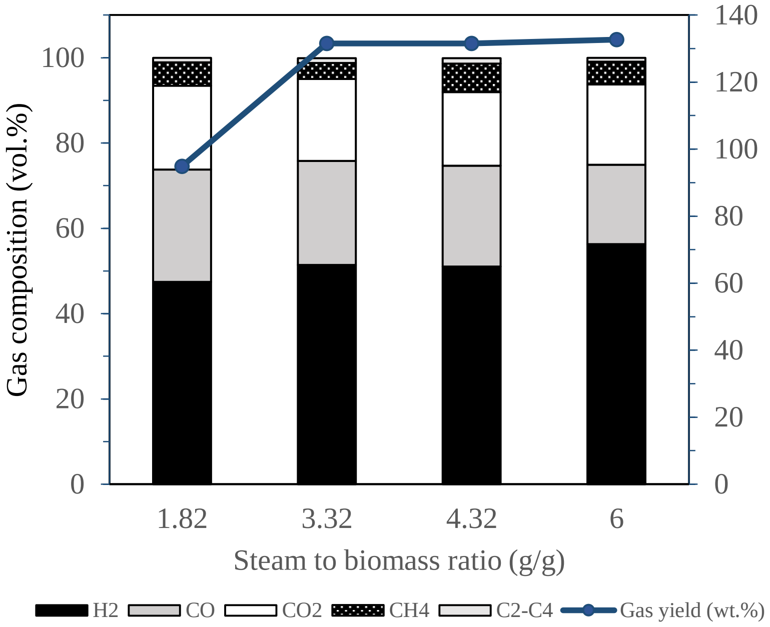
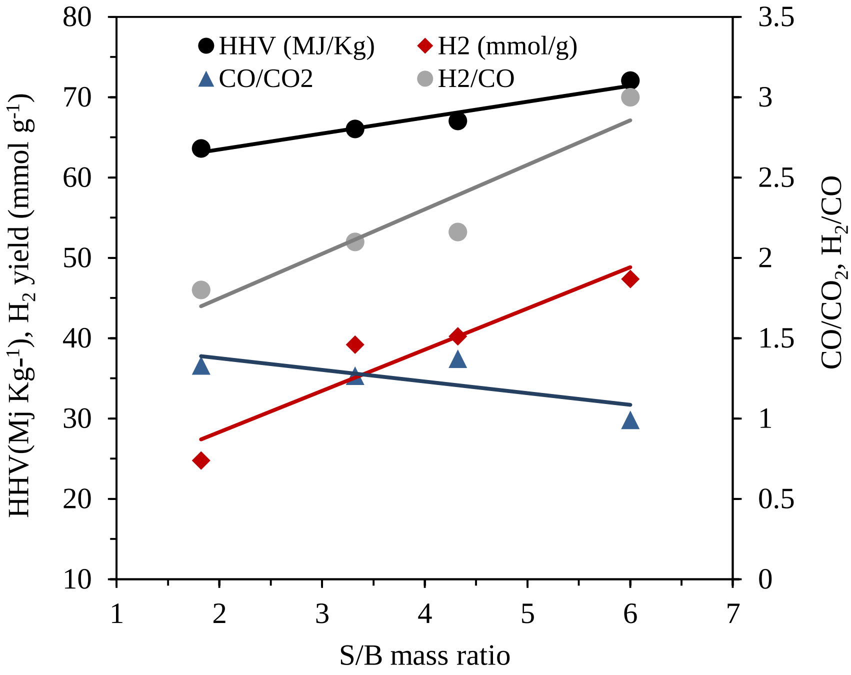


Fig. 4. The influence of steam to biomass (S/B) ratio on gas composition and total gas yield



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672 **Fig. 5.** Effect of steam to biomass ratio on H_2yield, HHV, H_2/CO and CO/CO_2.

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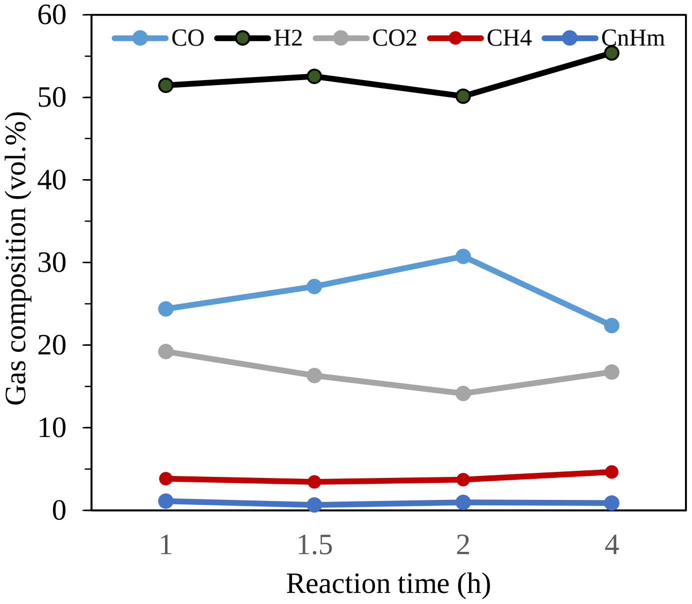

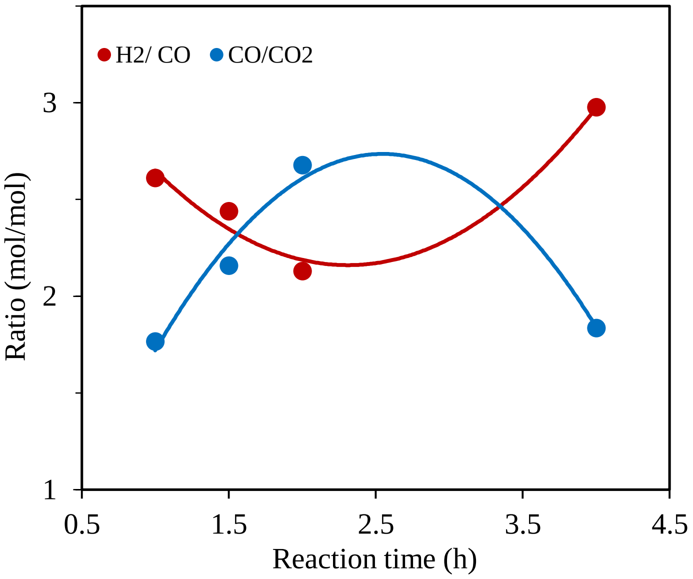

Fig. 6. The influence of reaction time on the product gas compositions and H_2/CO and CO/CO_2 ratios in the syngas

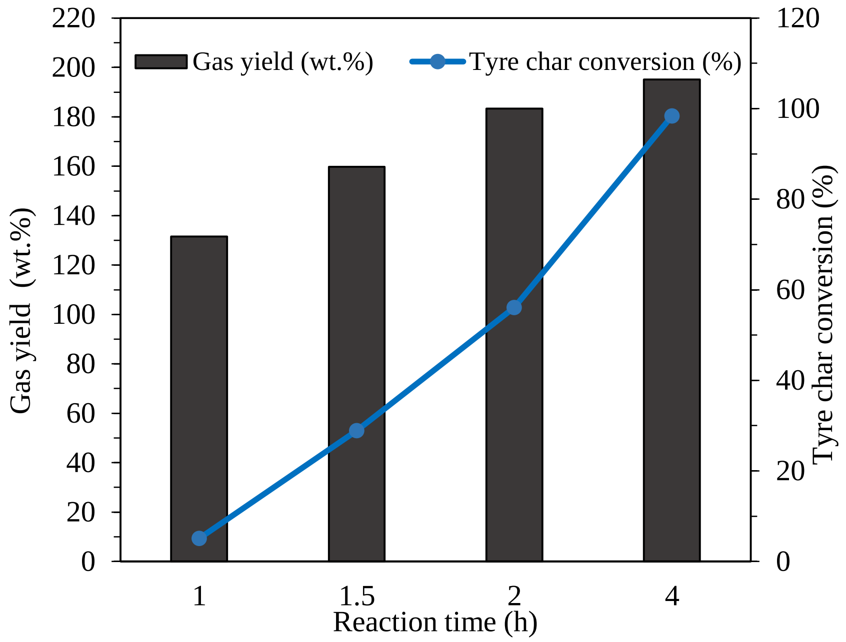

Fig. 7. The influence of reaction time on tyre char conversion and total gas yield for biomass pyrolysis-tyre char gasification.

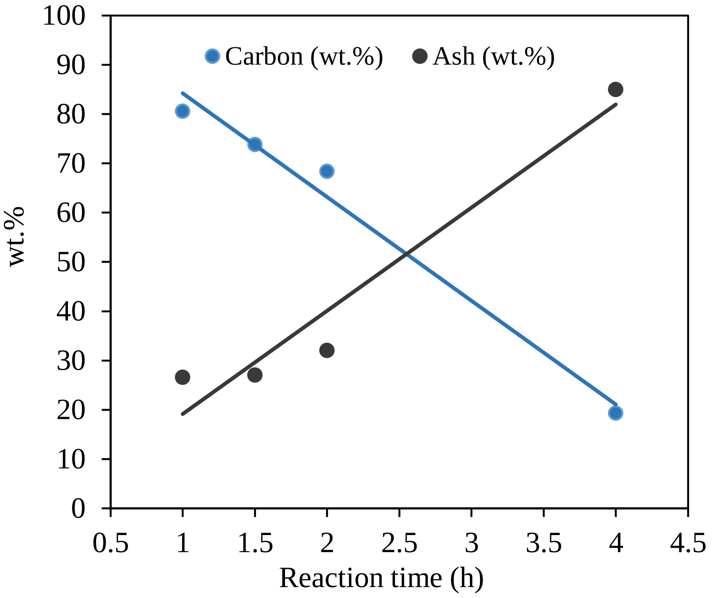

Fig. 8. Carbon and ash content of tyre char from catalytic gasification of biomass at different reaction times