Applied Energy 190 (2017) 501–509

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

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

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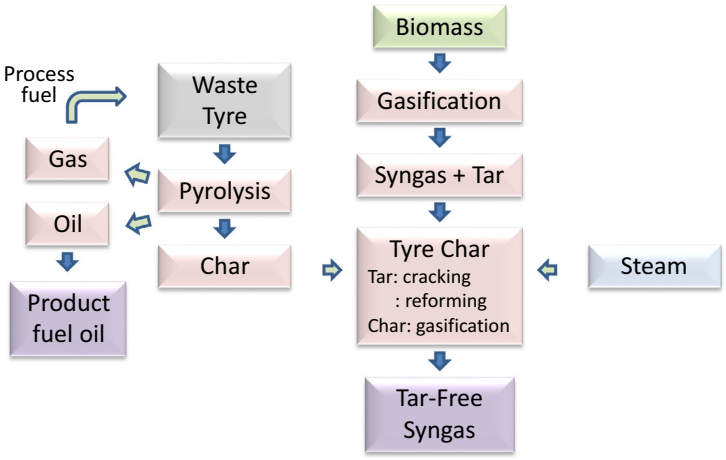
HIGHLIGHTS

- Tyre char is used as catalyst and syngas source in pyrolysis-reforming of biomass.
- Metals in tyre char catalyse tar decomposition.
- Increased steam and higher temperature promotes H_2 production.
- Syngas H_2/CO ratio varied between 1.3 to 2.
- A waste derived catalyst degrades tar and is also sacrificed for char gasification.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 July 2016
Received in revised form 19 December 2016
Accepted 22 December 2016
Available online 7 January 2017

Keywords:
Waste tyre
Pyrolysis
Biomass gasification
Tar removal
Syngas

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 °C, 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). 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}).

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http://dx.doi.org/10.1016/j.apenergy.2016.12.099
0306-2619/

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 800 °C 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, Striūgas 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 °C 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 °C. 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 °C min^{-1} to a final temperature of 800 °C and held at that temperature for one hour. The recovered pyrolysis chars were ground and sieved to a particle size of ~1 mm and oven-dried for 24 h.