



Thermal decomposition and gasification of biomass pyrolysis gases using a hot bed of waste derived pyrolysis char



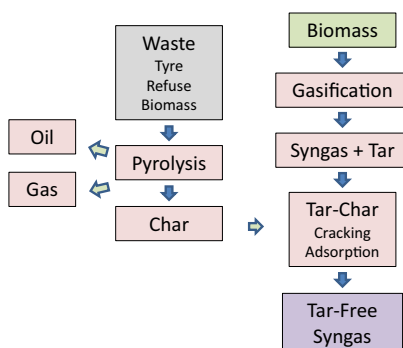
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HIGHLIGHTS

- Waste derived chars have been used to crack bio-oil/tar hydrocarbons.
- Wastes used were, scrap tyres, refuse derived fuel and biomass.
- Highest tar cracking was 70% with tyre-derived pyrolysis char.
- H₂ and CO₂ increased with the chars due to catalytic cracking of tars.
- Tar removal is due to catalytic conversion and physical adsorption.

GRAPHICAL ABSTRACT



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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.

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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 pro-

cesses 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

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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 CO₂ (Abu El-rub et al., 2008). For example, Abu El-rub et al. (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 CO₂ 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, CO₂, H₂O or O₂ introduced into the second stage reactor and different char temperatures of 700–1000 °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 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 CO₂. Therefore, although pyrolysis and char cracking may take place in an inert atmosphere of nitrogen or argon (Sun et al., 2011; Gilbert et al., 2009), the pyrolysis of biomass will produce a partial oxidation atmosphere through the formation of steam and CO₂ as reaction products which can react with the char to produce CO, CO₂, H₂.

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 600–800 °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. 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

Table 1
Composition of the raw waste materials.

Analysis (wt.%)	Tyre	RDF	Date stones
<i>Proximate analysis</i>			
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	13.0	69.9
<i>Ultimate analysis</i>			
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

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