



Effects of volatile–char interactions on *in situ* destruction of nascent tar during the pyrolysis and gasification of biomass. Part I. Roles of nascent char



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HIGHLIGHTS

- Volatile–char interactions can result in tar destruction during pyrolysis.
- The effects of char on tar destruction are not proportional to the amount of char.
- O-containing functional groups in char enhance tar destruction.
- Aromatic ring size and substitutional groups in tar are important for tar destruction.

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ABSTRACT

This study aims to investigate the roles of char in the *in situ* destruction of tar during the volatile–char interactions. Rice straw and water/acid-washed rice straw samples were pyrolysed at 850 °C with controlled extents of volatile–char interactions in a fluidised-bed/fixed-bed reactor. Our results indicate that the amount of tar decreases significantly with increasing extent of volatile–char interactions. The nascent char has a positive effect on tar destruction, although the effect is not proportional to the amount of char. The destruction of tar compounds during the volatile–char interactions varies with the functional groups, ring sizes and ring structures of tar molecules. Washing the raw biomass with water or acid also changes the extent of tar destruction during the volatile–char interactions. Our results indicate that the char structural features such as the O-containing groups on the char surface are an important factor influencing the tar destruction during the volatile–char interactions.

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1. Introduction

Biomass gasification is one of the attractive technologies to utilise biomass for chemical production or power generation [1–3]. However, the existence of tar in the product syngas can cause many troubles for the downstream equipment [4–6]. Thus, one of the major challenges for the commercialisation of biomass gasification technologies is to find an economic and effective way to eliminate the refractory tar in the product gas.

Among the approaches for tar destruction, catalytic cracking/reforming is gaining widespread acceptance due to its overall high energy efficiency [6–8]. A number of materials have been tested as catalysts, but a number of problems still exist hindering their commercial use, including high cost, low activity and ease to be

poisoned/deactivated [9–15]. Char, a cheap material from the pyrolysis/gasification of coal/biomass, could have high activity to destruct tar [16–27]. Another advantage of char as a tar cracking/reforming catalyst is that the deactivated char catalyst can easily be burned or gasified to recover its energy without the need of regeneration.

It should be noticed that the “char catalysts” for tar cracking in the previous studies (see above) have already experienced some extent of volatile–char interactions during their preparation from coal/biomass in a pyrolyzer/gasifier. It is known that the volatile–char interactions have significant effects on the volatilisation of alkali and alkaline earth metallic (AAEM) species from char [28–31] and the evolution of char structure [32–34]. However, it is still not clear if the changes to char caused by the volatile–char interactions will lead to some differences in the performances of tar cracking between the “nascent char” and relatively “older char”; the

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latter has experienced very different extents of volatile–char interactions from the former.

In fact, the volatile–char interactions are a common phenomenon in any type of gasifiers. In some gasifiers (e.g. fluidised-bed gasifiers), the char particles would continuously interact strongly with volatiles. The nascent char particles have great potentials to destruct nascent tar vapours during the volatile–char interactions [35–37]. However, the exact mechanisms of tar destruction during the volatile–char interactions remain unclear. In particular, little is known about the relative importance of char structure on tar destruction. This information is particularly important for biomass gasification because the chars from biomass usually have amorphous structures [34,38], making these chars particularly reactive during volatile–char interactions.

This series of papers aim to investigate the effects of volatile–char interactions on the *in situ* destruction of tar during the pyrolysis and gasification of biomass. The first paper focuses mainly on the roles of nascent char in the destruction of tar during volatile–char interactions.

2. Experimental

2.1. Biomass samples

As a typical agricultural waste with great potential for gasification, rice straw from Wuhan area (China) was used in this study. The raw straw was pulverised with a laboratory mill and sieved to the particle sizes ranging from 90 to 180 μm . The proximate and ultimate analyses of the rice straw sample are given in Table 1. The biomass sample was stored in air tight containers in a freezer to avoid oxidation or biological activities.

A part of the rice straw sample was washed with deionised water or dilute nitric acid (0.1 wt.%) following our previous procedures [39]. Briefly, the rice straw sample was immersed in water or acid (10 ml per g of biomass) at room temperature for 2 h, after which the sample was rinsed with deionised water to neutral. The untreated rice straw (RS), water-washed rice straw (WRS) and acid-washed rice straw (ARS) samples were all dried at 105 $^{\circ}\text{C}$ overnight before pyrolysis experiments.

2.2. Fast pyrolysis

A three-frit two-stage fluidised-bed/fixed-bed quartz reactor [25,30] was used for the fast pyrolysis of biomass. The main reactor body is 37 mm in diameter and the top and bottom stages are 30 and 130 mm in length respectively. About 70 g of silica sand (212–300 μm) was used as the fluidised bed material in the bottom stage of the reactor. Argon (>99.999%) was used as the feeding gas and fluidising gas, with the flow rates of 1.00 L min^{-1} and 0.72 L min^{-1} , respectively. After the reactor had stabilised at the target temperature (850 $^{\circ}\text{C}$), biomass particles were entrained from the feeder by the feeding gas and fed into the fluidised bed

at a rate of about 100 mg min^{-1} through an injection probe, which was cooled with running water (1 L min^{-1}) to avoid the heating of biomass particles before they entered the fluidised bed.

Once fed into the fluidised bed, biomass would be heated up very rapidly at a rate $>10^3\text{--}10^4 \text{K s}^{-1}$ [40] and underwent pyrolysis to generate volatiles and char. Under our experiment conditions, the flow rate was high so that the char particles were elutriated out of the sand bed to form a thin char bed underneath the middle frit [25,30] in the reactor. With the continuous feeding of biomass, nascent volatiles would have to pass through and interact with this nascent char bed, the height of which can be controlled by the amount of biomass fed into the reactor. Therefore, the extent of volatile–char interactions can be controlled during pyrolysis by the length of time of feeding (i.e. the time when volatiles are generated to interact with char) and the biomass feeding rate (i.e. the concentration of volatiles interacting with the char).

Once the pre-set amount of biomass was fed into the reactor, pyrolysis was terminated by stopping the feeding and lifting the whole reactor out of the furnace to be cooled down naturally in the ambient air. Argon was still passing through the reactor to avoid any oxidation until the reactor was completely cooled down to room temperature.

2.3. Sampling and analysis of tar

2.3.1. Tar sampling and determination of tar yield

The product gases from pyrolysis exited the reactor outlet and passed through three traps containing the HPLC-grade chloroform and methanol mixture (4:1 by vol.) cooled in ice-water bath (0 $^{\circ}\text{C}$) (the first trap) and dry ice baths (the second and third traps), as described previously [25,40,41]. All the recovered tar solutions from the three traps were mixed and weighed before being stored in a freezer.

The “tar yield” is experimentally defined as the material dissolved in the chloroform and methanol mixture but not evaporated at 35 $^{\circ}\text{C}$ within 4 h. The determination method has been described elsewhere [25,40–42].

2.3.2. GC–MS

The tar solutions were analysed by Agilent GC–MS (a 6890 series GC plus a 5973 MS detector) to understand the behaviour of relatively light tar components during pyrolysis. A detailed description of the instrument and method can be found elsewhere [41]. The identification of the unknown compounds was based on the matches of their retention times and MS spectra with those of the standards injected and/or those in the National Institute of Standards and Technology (NIST) library. The standards injected were toluene, styrene, indene, naphthalene, phenol, dibenzofuran, acenaphthylene, fluorene, phenanthrene, anthracene and fluoranthene.

Table 1
Properties of biomass samples used in this study.

	Proximate analysis (wt.%, db)		Ultimate analysis (wt.%, daf)				
	Volatile matter	Ash	C	H	N	S	O
Untreated rice straw	67.8	13.6	48.7	6.3	1.0	0.2	43.9
	Contents of key inorganic species (wt.%, db)						
	Na	K	Mg	Ca	Al	Fe	
Untreated rice straw	0.032	2.325	0.307	0.595	0.014	0.015	
Water-washed rice straw	0.016	1.112	0.244	0.588	0.014	0.014	
Acid-washed rice straw	0.003	0.167	0.139	0.562	0.014	0.012	

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