



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



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HIGHLIGHTS

- Steam can reform larger aromatics more easily than smaller ones in the gas phase.
- Steam enhances the tar destruction during the volatile–char interactions.
- Steam–char reactions produce additional active sites to facilitate tar destruction.

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ABSTRACT

This study aims to investigate the importance of steam to tar destruction during the volatile–char interactions. Steam was supplied in the absence and presence of nascent char during the pyrolysis/gasification of biomass at 850 °C. In the absence of char, steam has more significant effects on the reforming of large aromatic ring systems (e.g. >2 fused benzene rings) than small and isolated aromatics. In the presence of char, steam can significantly enhance the reforming of both large and small aromatic ring systems during the volatile–char interactions, especially when the steam–char reactions are also significant. The results indicate that the steam–char reactions are particularly inhibited in a thin char bed by the volatile–char interactions. It is believed that the steam–char reactions can produce additional active sites on the char, such as the radicals/intermediates of char gasification and/or the O-containing groups, to facilitate tar reforming during the volatile–char interactions.

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1. Introduction

As an undesirable product from the gasification of biomass [1–4], tar can be dealt with by physical separation or catalytic reforming after gasification [5–8]. Alternatively, it may be cheaper to minimise the formation of tar during gasification. In fact, tar formation and destruction are complicated processes involving a network of reactions [9–19] in the gas phase, solid phase and at the gas–solid interface. The pyrolysis of biomass will generate substantial amounts of volatiles with abundant radicals and a vulnerable nascent char, which can react with each other [20–24]. The volatile–char interactions can affect almost every aspect of reactions during pyrolysis and gasification, including the volatilisation of alkali and alkaline earth metallic (AAEM) species from the char [21], the gasification of char [22], the change in char structure [23],

and the destruction of tar [24]. These reactions will become more complicated in the presence of steam.

Steam is a commonly used gasifying agent to produce high quality syngas [25,26]. Steam can participate in various reactions such as the reforming of tar/gaseous hydrocarbons, water–gas shift reactions and char gasification. Although there is some information about the effects of steam on tar destruction during gasification [26–34], a good understanding of the roles of steam in the evolution of tar during each of the simultaneous reactions has not yet been achieved. In particular, little is known about the relative importance of steam to the tar destruction in different phases in the presence of the volatile–char interactions.

Our first paper in this series [24] investigated the *in-situ* destruction of nascent tar during the volatile–char interactions, particularly the importance of char structure to the *in-situ* tar destruction. As steam can cause drastic changes to the char structures [35,36] in addition to its roles in tar reforming and char gasification, it is postulated that steam may both directly and

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indirectly affect the tar destruction during the volatile–char interactions via its effects on tar reforming reactions and relevant char reactions.

This paper examines the roles of steam in the tar reforming reactions in the gas phase, the reactions involving char and the tar destruction through the volatile–char interactions, aiming to reveal the relative importance of steam in each aspect of tar destruction during the volatile–char interactions.

2. Experimental

2.1. Destruction of biomass tar with steam supply in two different modes

In this study, the pyrolysis of rice straw at 850 °C done in Part I [24] was taken as the control experiments, which are denoted as the “Pyrolysis” mode in this paper. The rice straw samples (90–180 μm), the three-frit two-stage fluidised-bed/fixed-bed quartz reactor [21,24,37] and the operations used in this work were all the same as those in Part I [24], except that steam was injected in this paper (15 vol.% of the total gas flow rate). Briefly, after the reactor had stabilised at 850 °C, biomass was continuously fed into the fluidised bed at a rate of about 100 mg min⁻¹ to undergo the fast pyrolysis in argon (>99.999%) atmosphere. At the same time, steam was injected by directly feeding water into the reactor with a high performance liquid chromatography (HPLC) pump.

As is shown in Fig. 1, steam was supplied in two different ways: in the absence of char (“Reforming without char” mode) and in the presence of char (“Reforming with char” mode). Due to the presence of the middle frit [21,24,37], the reaction zone was divided into two stages. Biomass was pyrolysed in the bottom stage to generate the volatiles and char. The char was elutriated out of the sand and captured by the middle frit to form a thin char bed. In the “Reforming without char” mode, steam was injected in the top stage where no char was present, thus, steam could only have, if any, effects on the gas-phase reactions in the top stage. In the

“Reforming with char” mode, steam was injected into the bottom stage just underneath the char bed to take part in both the volatile–char interactions in the bottom stage and the gas-phase reactions in the top stage. Therefore, by comparing the tar of the “Reforming without char” mode with that of the “Pyrolysis” mode and by comparing the tar of the “Reforming with char” mode with that of the “Reforming without char” mode, we could examine the roles of steam in tar destruction in the gas phase and during the volatile–char interactions.

2.2. Characterisation of tar and char

The product tar was trapped by three tar traps containing a chloroform and methanol mixture (HPLC-grade, 4:1 by vol.) [37,38]. UV-fluorescence spectroscopy was used to trace the evolution of aromatic ring systems in tar samples. The details of the instrument configuration and analysis method have been described previously [37,38]. The fluorescence intensity was expressed on the basis of “per gram of biomass (db)” [38–40].

The tar samples were also analysed by Agilent GC–MS (a 6890 series GC with a 5973 MS detector) with the details given elsewhere [40]. A series of standards [24] were used to identify and quantify the tar compounds detected by GC–MS. The yields of the selected tar compounds were shown on the basis of “per gram of biomass (db)”.

The weight difference of the reactor before and after each experiment was taken as the mass of char and then used to calculate the char yield. The char structural features were characterised with a Perkin–Elmer Spectrum GX FT-IR/Raman spectrometer [41,42]. The configuration of instrument and the method of sample preparation were the same as that in Part I [24]. Each Raman spectrum (800–1800 cm⁻¹) was deconvoluted into 10 Gaussian bands using the GRAMS/32 AI software. A detailed discussion of the band assignment can be found elsewhere [41–43]. Generally, the ratio of $I_{(GR+VL+VR)}/I_D$ was used to reflect the ratio between small and large aromatic ring systems in chars [41–43].

3. Results and discussion

3.1. Effects of steam on tar reforming in the gas phase

Fig. 2 shows the UV-fluorescence spectra of tars from different modes for different amounts of biomass fed into the reactor. The shapes of all spectra were similar, indicating that the types of aromatic ring structures were also similar in these tars. As the fluorescence intensity was shown on the basis of “per gram of biomass (db)”, it was taken to reflect the “yields” of aromatic ring systems in tars produced under different experimental conditions. For each given amount of biomass fed (Fig. 2a–d), injecting steam into the gas phase (“Reforming without char” mode) could result in lower “yields” of aromatic ring systems than pyrolysis (“Pyrolysis” mode). It should be noticed here that the actual amounts of biomass fed could vary slightly for each targeted amount of biomass to be fed. In order to make the comparison clearer between different modes, the peak areas of UV-fluorescence spectra were further used as a semi-quantitative reflection of the “yields” of aromatic ring systems as a function of both reaction mode chosen and amount of biomass fed, as is shown in Fig. 3a. The trends in Fig. 3a clearly showed consistently lower peak areas for the “Reforming without char” mode than those for the “Pyrolysis” mode. As steam was supplied into the top stage of the reactor in the absence of any char particles, it was clear that steam could have some effects on the reforming of the aromatic ring systems in the gas phase.

In addition, the “yields” of aromatic ring systems in the “Reforming without char” mode and “Pyrolysis” mode both

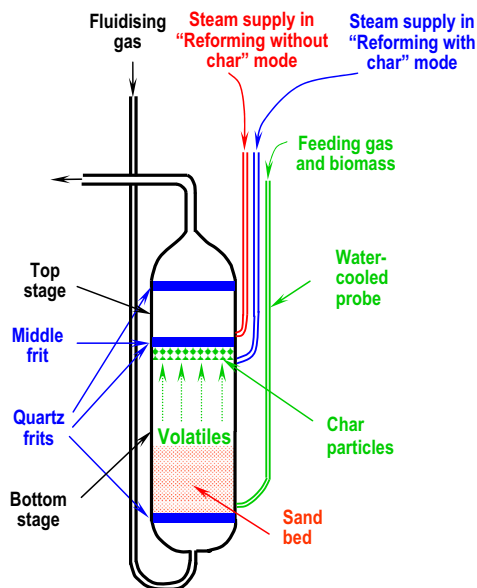


Fig. 1. A schematic diagram of the two-stage fluidised-bed/fixed-bed quartz reactor (reprinted and modified from Ref. [21] with permission from Elsevier) and the two different ways of steam supply: In the “Reforming without char” mode, steam was supplied in the top stage without the presence of any char particles; in the “Reforming with char” mode, steam was supplied in the bottom stage just underneath the char bed to participate in the volatile–char interactions.

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