



## Research article

## Destruction of tar during volatile-char interactions at low temperature

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## ABSTRACT

This study aims to investigate the mechanisms of tar destruction during volatile-char interactions at low temperature (400–700 °C). A bio-char was subjected to interactions with biomass volatiles at different temperatures (400–700 °C). The results indicate that tar is converted into gaseous and solid products (coke) during volatile-char interactions and the proportion of coke formed on the bio-char from the total converted tar steadily increases with increasing temperature. The non-aromatic structures (e.g. aliphatic and/or O-containing structures) in tar are mainly converted into gases by catalytic cracking and/or reforming reactions on char, while the aromatic structures in tar primarily go through condensation/polymerisation reactions to form coke on char surface. The UV-fluorescence spectroscopic results imply that the non-aromatic structures in tar are easier converted on char than aromatic structures at low temperature (e.g. 400–500 °C) and the conversion of aromatic structures through coke formation on char will be enhanced at higher temperature (e.g. 600–700 °C). The Raman spectroscopic results show that some O-containing species in tar molecules are transferred to the char and form additional O-containing structures into the entire char matrix during the volatile-char interactions.

## 1. Introduction

The volatile-char interactions are an important phenomenon during the pyrolysis and gasification of low-rank fuels (e.g. biomass/coal) [1]. When fuel particles are subjected to high temperature, nascent volatiles are released and a solid char is formed. The char particles are inevitably surrounded by volatiles including the condensable large molecules (tar), the non-condensable small molecules (gases) and the radicals from the cracking/reforming of tar/gases. In terms of tar evolution, the interactions between volatiles and char have serious implications both for pyrolysis and gasification.

Regarding to pyrolysis technology generally operated in a low temperature range (e.g. 400–600 °C) [2–5], the volatile-char interactions may have some detrimental effects on the bio-oil production, especially in reactors where volatile-char interactions are constantly in presence, such as a fluidised-bed reactor [6,7]. As char can have catalytic effect on cracking volatiles at low temperatures [8,9], the yield of bio-oil is expected to be reduced by intensive volatile-char interactions. Moreover, the bio-oil composition may also change with the extents of volatile-char interactions in different operating conditions.

In the point view of gasification, the destruction of tar using char as a catalyst [8,10–14] has been an attractive option to tackle the tar-related problems [15–18], especially for the biomass gasification. Normally, the destruction of tar by char as a catalyst has been widely

studied in high temperature ranges (e.g. > 700 °C) [19–22]. Nonetheless, there are also circumstances that tar reduction can be operated at lower temperatures (e.g. ≤ 700 °C). For instance, the temperature in the tar reduction unit (e.g. a catalyst bed after gasifier) can be even lower if a low-temperature gasification route (e.g. < 800 °C) is adopted, which is advantageous in terms of cost and operation (e.g. higher cold gas efficiency, lower energy consumption and lessened ash-related problems compared with high-temperature gasification) [23,24].

Therefore, the evolution of tar (bio-oil) during volatile-char interactions are imperative for the design and operation of the gasification/pyrolysis technologies. Unfortunately, a good understanding about this phenomenon at low temperature has not been reached. Coke is a highly probable product from tar conversion on char in addition to some gaseous products at low temperature (e.g. 400–700 °C) [8,9,25,26]. However, little is known about the relative significance of the coke formation and gas evolution during tar conversion on char at low temperature (e.g. 400–700 °C). Furthermore, the effects of tar structural features on the formation of coke and gases during volatile-char interactions remain unclear.

In this paper, a biochar was subjected to interactions with volatiles from biomass at low temperature (400–700 °C). Some key parameters, such as temperature and tar structural features were studied to examine their effects on the destruction of tar during volatile-char interactions.

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The changes in the structural features for both tar and char during volatile-char interactions were also characterised, thereby providing further information to explore the relevant reaction pathways.

## 2. Methodology

### 2.1. Preparation of bio-char

Rice straw with a particle size range of 90–180  $\mu\text{m}$  was used to prepare the bio-char using a three-frit two-stage fluidised-bed/fixed-bed quartz reactor [27]. The reactor is 37 mm in diameter; and the lengths for the top and bottom stages are 30 mm and 130 mm, respectively. The properties of rice straw were as follows: C, 48.7; H, 6.3; N, 1.0; S, 0.2; O, 43.9 wt% (daf); VM, 67.9; and ash, 13.6 wt% (db) [13]. Briefly, rice straw (about 3 g per batch) was pre-loaded into the bottom stage of reactor and then heated up to 800  $^{\circ}\text{C}$  at a heating rate about 15  $^{\circ}\text{C}/\text{min}$  with a continuous flow of argon (99.999%). The reactor was held for 10 min after it had stabilised at 800  $^{\circ}\text{C}$  to complete the decomposition of rice straw particles. Finally, the reactor was lifted out of the furnace and cooled down to the room temperature in argon atmosphere. As the bio-char was prepared at high temperature (800  $^{\circ}\text{C}$ ), it would be difficult to undergo further ring condensation reactions due to thermal effects at lower temperatures (400–700  $^{\circ}\text{C}$ ) [28]. Thus, the differences in the structures of fresh bio-char used at different temperatures (400–700  $^{\circ}\text{C}$ ) would be minimised.

### 2.2. Tar destruction during volatile-char interactions

The same reactor mentioned above [27] was used in a separate series of experiments for volatile-char interactions. Briefly, mallee wood (90–180  $\mu\text{m}$ , Western Australia) was fast pyrolysed in a fluidised-bed at the bottom stage of reactor to generate volatiles and char. The char particles of mallee wood would be intercepted by the middle frit (separating the reactor into top and bottom stages), while the volatiles would pass through this frit and entered the top stage, where the bio-char (from rice straw) was pre-loaded in the top stage of reactor. Thus, the volatiles of mallee wood would have to interact with the bio-char (from rice straw) at various temperatures (400–700  $^{\circ}\text{C}$ ). More experiment details are described as follows.

The properties of mallee wood are given below: C, 48.2; H, 6.1; N, 0.15; S, 0.01; Cl, 0.04; O, 45.5 wt% (daf); VM, 81.6; and ash, 0.9 wt% (db) [29]. About 1 g of bio-char (from rice straw) was pre-loaded into the top stage of the reactor as a fixed-bed before being heated up. About 60 g of silica sand (212–300  $\mu\text{m}$ ) was used as the fluidised-bed material in the bottom stage of reactor. Argon (> 99.999%) was used as the feeding gas (1.35  $\text{L min}^{-1}$ ) to entrain biomass particles into the bottom stage of reactor. The flow rate of fluidising gas (argon, > 99.999%) at reactor bottom was adjusted between 0.63 and 1.52  $\text{L min}^{-1}$  to ensure the same residence time for volatiles passing through the char bed at different temperatures (400–700  $^{\circ}\text{C}$ ).

After the reactor had stabilised at a pre-set target temperature (400–700  $^{\circ}\text{C}$ ), mallee wood particles were fed into the fluidised bed at the bottom stage of reactor at a rate of about 75 mg/min through an injection probe, which was cooled by running water (about 1  $\text{L min}^{-1}$ ) to avoid the heating of biomass particles before they entered the fluidised sand bed. Then, the nascent volatiles from the fast pyrolysis of mallee wood would enter the top stage and pass through the fixed bed of bio-char. After the completion of feeding, the reactor was lifted out of the furnace and cooled down to room temperature with a continuous argon flow.

The yield of total solid products (including the char from pyrolysis of mallee wood at the bottom stage of reactor and, if any, the coke formed on the bio-char from mallee tars at the top stage of reactor) were measured by weighing the reactor before and after the experiment. In order to examine the char yield of mallee wood itself, blank experiments were carried out by pyrolysing mallee wood without pre-

loading bio-char (from rice straw) at the top stage of reactor.

Hence, the coke yield formed on the bio-char surface during tar destruction is calculated by Eq. (1).

$$\text{Coke yield\%} = \frac{\Delta M_{\text{reactor}} - M_{\text{biomass char}}}{M_{\text{biomass}}} \times 100\% \quad (1)$$

$\Delta M_{\text{reactor}}$ : the mass difference of the reactor before and after the experiment with the bio-char;

$M_{\text{biomass char}}$ : the mass of char from pyrolysis of mallee wood determined in blank experiment (without bio-char at the top stage of reactor).

$M_{\text{biomass}}$ : the mass of mallee wood fed into the reactor.

### 2.3. Sampling and analysis of tar

Tar was captured during each experiment with three traps containing a mixture of HPLC grade chloroform and methanol (4:1 by vol) in the ice-water and dry ice baths [14,29]. Tar yield was determined by quantifying the tar concentration in a given amount of tar solution evaporated at 35  $^{\circ}\text{C}$  for 4 h [29,30].

UV-fluorescence spectroscopy (using a Perkin-Elmer LS50B spectrometer) was used to characterise the aromatic structures in the tars following the experimental details given previously [14,29]. The fluorescence intensity was either shown on the basis of the same tar concentration (4 ppm) or shown on the basis of “per gram of biomass (db)” [31]: the former is derived directly from the original fluorescence spectra of the 4 ppm tar solutions, while the latter is derived by multiplying fluorescence density at 4 ppm tar solutions by the tar yield to semi-quantitatively reflects the yields of aromatic structures in tar per gram of biomass [14,29,31].

The tar solutions were also analysed by Agilent GC–MS (a 6890 series GC with 5973 MS detector) to understand the behavior of relatively light tar components during the experiments. The details of the instrument and method were described elsewhere [32]. The identification of the peaks in the chromatogram was based on the retention times and the MS spectra of the standards injected and/or the comparison with the National Institute of Standards and Technology (NIST) library.

### 2.4. Characterisation of the bio-char

The structural features of fresh and spent bio-char were characterised using a Perkin-Elmer Spectrum GX FT-IR/Raman spectrometer. The configuration of instrument and the sample preparation was described elsewhere [33,34]. Briefly, the Raman spectra ranged from 800 to 1800  $\text{cm}^{-1}$  were deconvoluted into 10 bands using the GRAMS/32 AI software with detailed discussion of band assignment given previously [33–35]. Generally, the Gr, Vl and Vr bands mainly represent small aromatic ring systems (3–5 fused rings) and other amorphous structures in chars, while the D band mainly represents the large aromatic ring systems (not < 6 fused rings). Hence, the ratio of  $I_{(\text{Gr} + \text{Vl} + \text{Vr})}/I_{\text{D}}$  is used to express the ratio between small and large aromatic ring systems in char.

## 3. Results and discussion

### 3.1. Effects of temperature on the distribution of products from tar conversion during volatile-char interactions

Fig. 1 shows the yields of tar from the pyrolysis of mallee wood with/without the bio-char at different temperatures. It was found that tar yields in the absence of bio-char decreased with increasing temperature, especially when temperature was higher than 500  $^{\circ}\text{C}$ . The results show that the thermal cracking of tar in gas phase mainly became significant when temperature was above 500  $^{\circ}\text{C}$ . However, when subjected to the bio-char, significant reduction in tar yields due to the

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