

Insights on the role of secondary tar reactions in soot inception during fast pyrolysis of coal

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Introduction

Coal pyrolysis has been studied extensively for more than a century. However, due to complexity of the chemistry and of transportation phenomena involved, no general mechanism is universally accepted, nor all observations can be accounted for by any single model [1]. Recent work from a collaboration of Bochum and Naples addressed the influence of environment gas atmosphere (N₂ and CO₂) on the early products of fast pyrolysis in a DTR at 1573 K of a high volatile bituminous coal [2]. As regards the char, it was found that the CO₂-char exhibited a lower reactivity compared to the N₂-char. Moreover, in CO₂ atmosphere the amount of submicronic fraction of carbon particulate, referred to as soot, was found to be up to four times as much as upon N₂ experiments [3]. Beside the larger formation of soot, relevant differences in terms of combustion reactivity, size distribution and chemical structure of the residual carbon particulate produced in CO₂ environment with respect to N₂ environment were observed [2].

The present paper reports data on the tar produced in the fast pyrolysis of the same coal in a DTR and also in a heated strip reactor (HSR). In the DTR particles heat up and pyrolyze in a hot gas environment. Differently, in the HSR the particles heat up on a hot carbon foil, the surrounding gaseous environment being at nearly ambient temperature. As a consequence, volatile pyrolysis products are released in a hot environment in the DTR and in a cold environment in the HSR, determining different paths of volatile matter evolution.

Experimental

Experiments have been carried out on Colombian Coal (CC) whose properties are reported in [2]. Samples have been pyrolyzed in atmospheres of N₂ and CO₂ using gases of chromatographic grade in two different reactors, namely a drop tube reactor and a heated strip reactor, which are shortly described in the following.

DTR: The reactor was designed for high heating rate and short residence times, comparable to de-volatilization conditions of pulverized fuel boilers. The fuel particles are fed through a water-cooled injection tube to avoid preterm exposure to heat or reaction atmosphere. A microwave-based plasma source is used to heat the gases to a pre-selected temperature. An oil-cooled probe was used to sample and quench reaction products. The exhaust gases pass through a Pyrex glass tube, where the tar condenses. A more detailed description of the system is given in Refs. [2,3].

HSR: The reactor is a special heated grid device, where the usual metal grid used as the sample holder is replaced by a pyrolytic graphite foil thermally stabilized for use up to 2773 K [4]. The apparatus is enclosed in a stainless-steel vessel which can be pressurized up to 12 bar. The temperature of the grid is set by changing the value of the voltage at the two extremes of the strip. Due to the very high heating rate of the HSR, the strip can be considered isothermal for the entire duration of the test. About 100 mg of particles have been laid on the strip. The

reactor is flushed with the test gas (either N₂ or CO₂) for 10 min with a high flow rate to remove any oxygen traces. After flushing, the pressure was increased to 2 bar. The strip has then been heated up to 1573-2073 K and the total reaction time is 3 s. Due to the very small particle size, the coal particles are quickly heated up by contact with the strip and radiation from the reactor cover and can be considered isothermal with the strip. Details on equipment and heating rate profiles is provided in [4]. A Pyrex glass support was positioned over the strip to intercept ejected volatiles. The bridge did not heat up being nearly transparent to thermal radiation, therefore, tars condensed as soon as they impact on it.

Products analysis: The tar samples were recovered by washing the glass tube placed downstream of the DTR and the glass support located above the HSR with acetone in ultrasonic bath. The acetone volume was reduced to 0.5 ml under vacuum for analysis by gas chromatography-mass spectrometry (GC-MS). Acetone was unable to dissolve all the material deposited on the glass tube (DTR) and on the glass support (HSR) and the insoluble fraction was dissolved in N-methyl pyrrolidinone (NMP) and named “heavy tar”. The heavy tar was characterized by Size Exclusion Chromatography (SEC) for obtaining a molecular weight (MW) distribution and by UV-visible absorption for having information on the aromatic moieties.

The soot and char samples were recovered from the solid samples collected at the filter in DTR and from the sample holder/strip at the end of the experiment by a separation procedure involving dispersion in ethanol by ultrasonic mixing, followed by settling and decanting. The procedure produces top and bottom products constituted by coarse (char) and fine particle (soot) fractions, respectively as verified by SEM and granulometry [5].

Results

Fig. 1 reports the results of GC-MS analysis on HSR and DTR tars. The classes of species reported in figure are: light aliphatics (C7-C20), heavy aliphatics (C20-C30), oxygenated compounds (oxy) and PAH with different ring numbers (from 2 up to >5).

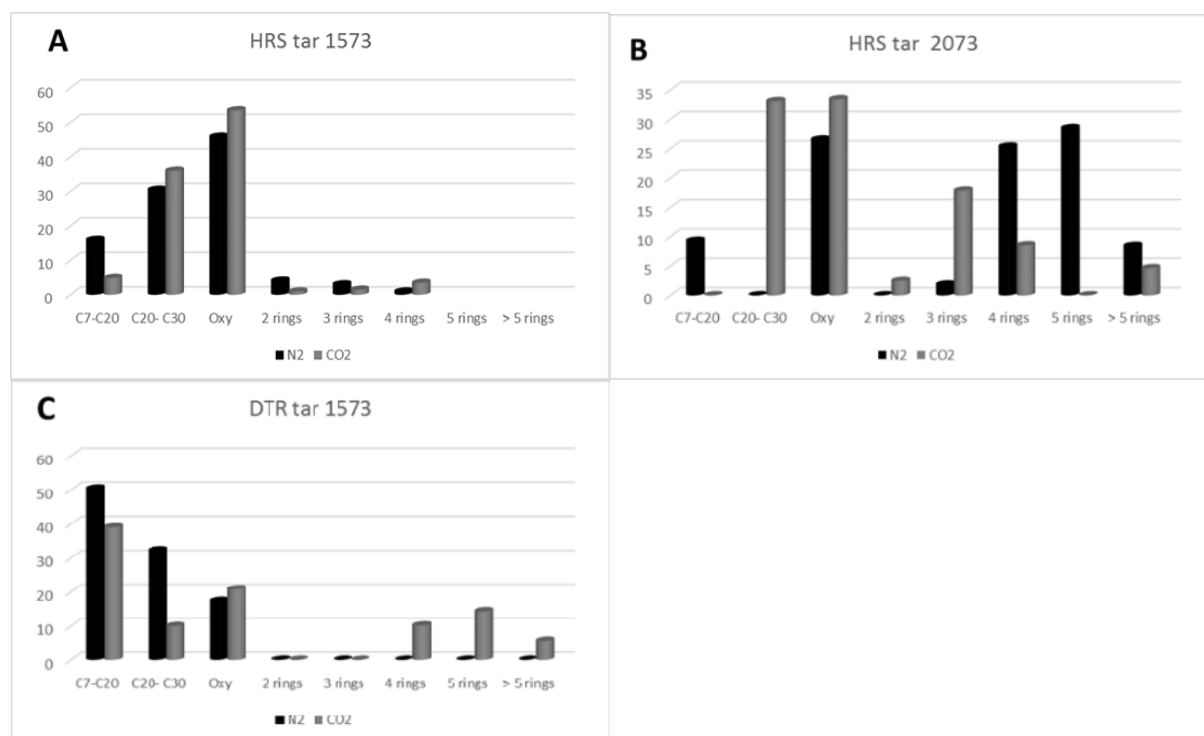


Figure 1. GC-MS analysis of tars collected in N₂ and CO₂ environment in HSR at 1573 K (a) and 2073 K (b), and in DTR at 1573 K (c).

It can be observed that the oxygenated compounds are the most abundant class in HSR system at 1573K whereas they are lower than aliphatics and comparable with PAH in the case of DTR system. Oxygenated compounds are comparable with heavy aliphatics in primary tar generated at 2073 K.

It can be assumed that the low temperature of the gas phase in the HSR limits the occurrence of secondary reactions of tar. This allows the formation of oxygenated species, limits cracking of heavy aliphatics in smaller aliphatics and, even more, their fragmentation in small hydrocarbons which participate in a series of H-abstraction, C₂H₂-addition steps to form benzenoid [6] and PAH of successively larger ring number, as in fuel-rich combustion [7]. By contrast, in DTR, the high temperature of the gas phase allows secondary reactions of tar and, as consequence, the small aliphatics and heavy PAH, mainly unsubstituted, including cata-annulated and peri-fused species, are more abundant.

The observation of Fig.1 suggests also a role of CO₂ in HSR at higher temperature and in DTR. Indeed, in HSR at 1573K the compositional distribution of tar is very similar in N₂ and CO₂, whereas at 2073K in CO₂ the composition presents less small aliphatics and less heavy PAH, suggesting an inhibition of aromatic growth by CO₂. By contrast, in DTR the CO₂ largely promotes PAH and heavy PAH formation with respect to N₂, which is consistent with the larger soot formation found in previous work [3]. The effect of CO₂ on char properties in dependence of the operative conditions is discussed in a previous paper [8].

The heavy tar, which is insoluble in acetone and therefore not analyzable by GC-MS, was dissolved in NMP and analyzed by SEC (Fig.2A) and UV-visible spectroscopy (Fig.2B).

From Fig.2A it is observable that in HSR system the MW distribution of heavy tar is very similar with both the temperatures and environment gases. It reveals for all the samples a bimodality in MW range going from 100 up to $6 \cdot 10^7$ u and only in the case of HSR at 1573K in CO₂ (Fig.2A) it is observable a slight decrease of the higher MW range. In DTR (Fig.2c) the distribution is essentially monomodal in the same MW range, with a shoulder shifter at higher MW with respect to HSR tar.

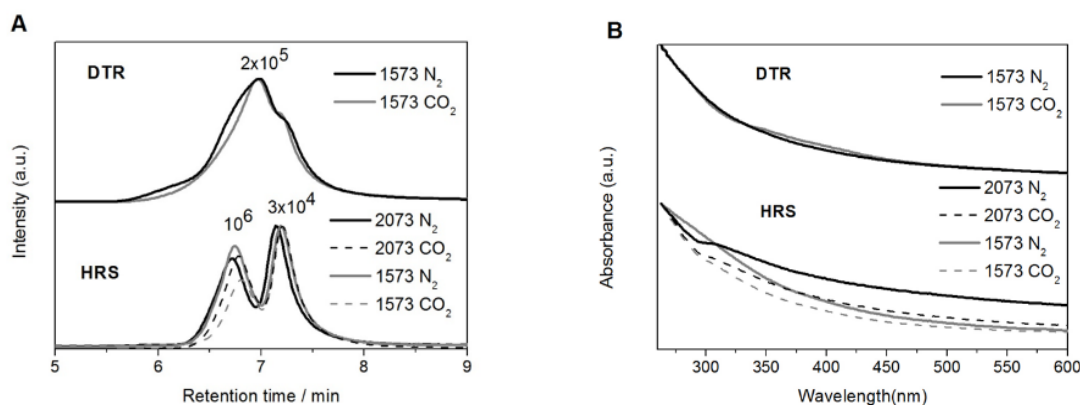


Figure 2. A) Normalized SEC profiles and B) Normalized Absorption spectra of heavy tars collected in N₂ and CO₂ in HSR and in DTR.

The UV-visible spectra of heavy tar of all samples reported in Fig.2B appear structure-less indicating the presence of aromatic moieties with bigger extension with respect to GC-MS PAH (up to 7 rings). They appear very similar among them regardless the temperature and the system, and the only notable difference is represented by HSR 2073 N₂ tar which shows a slope change and intensity increase of the spectrum after 300 nm. This feature suggests a heavier and more aromatic structure.

Conclusions

In the present work experiments in a HSR and a DTR allowed to investigate the effect of particles temperature, heating time, gaseous atmosphere and gas phase temperature on the tars produced from pyrolysis of Colombian Coal.

The results provide evidence that secondary reactions of the tar have a predominant role in formation of large PAH and soot inception. It is well known in literature that the degradation route rapidly increases with temperature along with aromatic growths [9]. The aromatic growth has a key role in soot formation [7], and, therefore, the much higher amount of soot formed from DTR with respect to HSR system confirms the hypothesis that soot from fast pyrolysis is formed from secondary reactions of tar [3 and references therein].

Acknowledgments

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