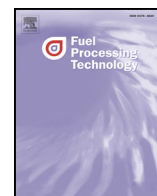




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## Fuel Processing Technology

journal homepage: [www.elsevier.com/locate/fuproc](http://www.elsevier.com/locate/fuproc)

Research article

## Coke formation during thermal reaction of tar from pyrolysis of a subbituminous coal

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## ARTICLE INFO

## Article history:

Received 15 January 2016

Received in revised form 15 March 2016

Accepted 19 March 2016

Available online xxx

## Keywords:

Tar

Coal pyrolysis

Volatiles reaction

Coke

Radicals

## ABSTRACT

The reaction of volatiles in a coal pyrolysis reactor determines the yield and quality of tar. This paper studies the yield, group composition and radical concentration of tars obtained from pyrolysis of a subbituminous coal, mainly on the effect of the tars' residence time in the pyrolysis reactor and in post-pyrolysis heating. The latter operation simulates the environment of tars, if they were in a large fast pyrolysis reactor. It is found that an increase in the volatiles' residence time in the pyrolysis reactor reduces the yield and increases the radical concentration of tars. The pitch fraction of the tars is mainly responsible for coke formation which occurs significantly at temperatures higher than 420 °C. The tars contain radicals, mainly in their coke and pitch fractions. The coke concentration in the tars increases with increasing heating time, linearly at 420 and 450 °C but in a sigmoidal pattern at higher temperatures. The coking behavior within 10 min can be expressed by the zero-order or zero-order + autocatalytic kinetics with activation energies of 128–138 kJ/mol.

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## 1. Introduction

Pyrolysis of low-and-mid rank coals at temperatures of 500–800 °C has long been regarded as an important route for the production of tar (including chemicals) and fuel gas, which are products or intermediates of high market value. Fast pyrolysis of coal attracted extensive attention in recent decades, especially in China, because it shortens the pyrolysis time and increases the tar yield. Many fast pyrolysis technologies were developed worldwide, but few were practiced on commercial scales. The common problems found include difficulties in dust/volatiles separation, high dust content in tar, difficulties in tar upgrading, as well as frequent clogging of volatile product lines and devices [1–3].

It is commonly accepted that these problems are resulted mainly from the reaction of volatiles as soon as they are formed from cleavage of weak covalent bonds in coals. The reaction of volatiles has been studied in various reactors and found responsible for low tar yield and high coke formation [1,4–7]. It was recently shown that the volatiles' reactions are mainly promoted by the high temperature environment surrounding the coal particles, which occurs in all types of pyrolysis reactors. The extent of the temperature increase experienced by the volatiles differs greatly in reactor type and configuration, from a few degree Kelvin (K) in a small fixed-bed reactor to a few hundred degree K in a fluidized-bed reactor or in a reactor that employs solid heat carriers [8]. These behaviors were recently attributed to the countercurrent flow of heat and volatiles in coal particles and in pyrolysis reactors [9].

The reaction of volatiles is very complex and affected by coal type, reactor configuration and pyrolysis conditions (such as heating rate,

carrier gas flow and pressure) [10–13]. Serio et al. [6] studied pyrolysis of Pittsburgh No. 8 coal (with a C content of 73.6 wt.%) in a two-stage fixed-bed reactor, with the first stage mainly for the generation of volatiles from the coal while the second stage solely for the reaction of volatiles. It was found that the tar yield changed with temperature and residence time of volatiles in the second stage. An increase in residence time from 0.6 to 1.1 s resulted in little change in tar yield at temperatures below 600 °C but a large change in tar yield at higher temperatures, about 30–50 wt.% reduction at 700–800 °C, for example. A first-order kinetics model was proposed for the tar loss. Doolan et al. [7] studied pyrolysis of Millmerran coal (with a C content of 79.1 wt.%) in a fluidized bed reactor and reported coke formation from volatiles although little quantification was given. Xu et al. [4] studied pyrolysis of Liddell coal (with a C content of 83.5 wt.%) in a two-stage fixed-bed reactor, with the second stage for the volatiles' reaction, and quantified the effects of temperature and residence time of volatiles in the second stage on the yields of tar, aliphatic and aromatic hydrocarbons and coke. It was found that the tar yield decreased while coke yield increased with increases in temperature and residence time. For example, the coke content increased from 1.2 wt.% (based on daf coal) at 500 °C to 4.9 wt.% at 900 °C at a residence time of 7 s. He et al. [1] simulated the reaction of volatiles by heating tars derived from pyrolysis of 4 coals (with C contents of 73.9–82.0 wt.%) in a small fixed-bed reactor. It was observed that the coke content of the tars increased with time at temperatures higher than 400 °C. It was also found that all the tars contained radicals (quantifiable by ESR) and the radical concentration increased with time at temperatures higher than 350 °C. The changes in coke yield were related with the changes in radical concentration, and the coking behavior was fitted by the second-order kinetics with activation energies of about 210 kJ/mol in a heating time range of 0.5–4 h.

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It is noted that the formation of coke in volatiles not only lowers the yield and quality of tar but also is responsible for clogging of the volatile product lines; it therefore plays an important role in feasibility and economy of a fast coal pyrolysis process. However, understanding of the volatiles' reaction in the literature is still rather limited, especially on quantifying the effects of temperature and residence time of volatiles on the yields and composition of tars and coke under the conditions of large scale pyrolysis reactors. Considering the dust/volatiles separation and tar processing or refining are also carried out at high temperatures the overall time of volatiles' reaction may range from seconds to a few minutes [14,15], it is important, therefore, to evaluate the coking behavior of volatiles and/or tars and their kinetics within this time range to meet the needs of design and operation of large scale fast pyrolysis reactors.

It is known that tar is a generic name of complex mixtures. Its composition has been practically presented in a simple way known as group composition, in which the group components are quantified in sequence by their solubility in solvents, such as hexane and tetrahydrofuran (THF) [16]. The hexane soluble fraction is light and termed oil, and is believed to be less responsible to coke formation. The hexane-insoluble but THF-soluble fraction is relatively heavy and termed pitch (including asphaltenes and preasphaltenes), and is found to be mainly responsible to coke formation [17–19]. The THF-insoluble fraction is termed coke. The differences in coke formation of oil and pitch fractions at high temperatures determine the yield and quality of tars. If the coke only come from the reaction of pitch, the yield of tar would decrease but the yield of oil would not be affected or even increase; if the oil converted to asphaltenes and then to coke, the yields of both tar and oil would decrease. Therefore, it is necessary to investigate the change of these tar components during the reactions of volatiles.

Based on the above analysis, this paper studies the reaction of tars collected from pyrolysis of a subbituminous coal in a fixed-bed reactor to simulate the reaction of volatiles in a large fast pyrolysis reactor. It includes the changes in tar components, radical concentration and coking behavior. Kinetics modeling of the coke formation in tars at high temperatures within a heating time of 10 min is also performed.

## 2. Experimental

### 2.1. Coal pyrolysis

The coal used was ground and sieved to 20–40 mesh for the pyrolysis experiments. Its proximate and ultimate analyses are listed in Table 1.

The pyrolysis was performed in a vertical fixed-bed quartz reactor ( $28 \times 580$  mm) coupled with a U-shaped quartz tube as shown in Fig. 1 under the ambient pressure. The U-tube was placed in a water-alcohol cold bath maintained at  $-13$  °C to condense tar in volatile products. The reactor loaded with 10 g coal was heated in the absence of the U-tube to  $110$  °C at a rate of  $10$  °C/min under an Ar ( $\geq 99.5\%$ ) flow and then maintained at the temperature for 1 h to remove the moisture in coal. The U-tube was then connected to the reactor and the coal was heated at the same rate to  $600$  °C. As soon as the temperature reached  $600$  °C, the reactor was removed from the heater and cooled down to room temperature. The char was weighed and its mass is termed

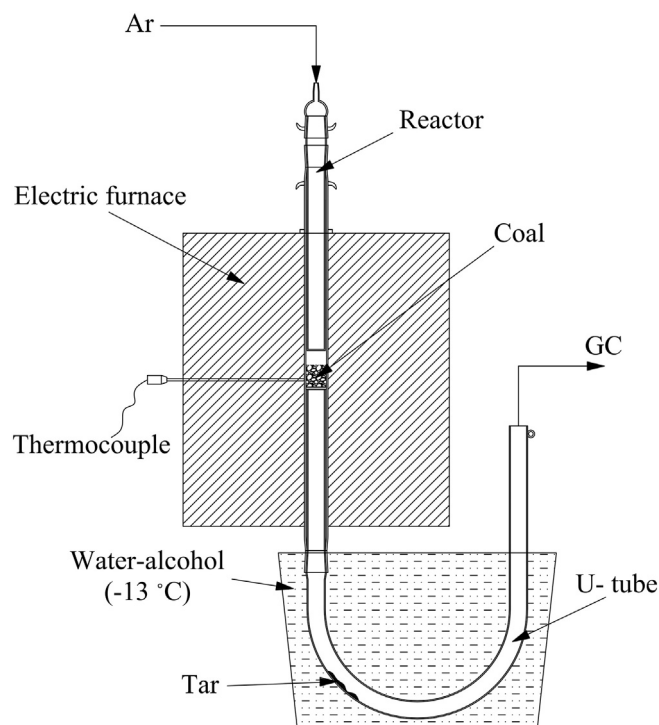


Fig. 1. Schematic diagram of the fixed-bed pyrolysis reactor.

$W_{\text{char}}$ . The mass of tar, termed  $W_{\text{tar}}$ , was determined by the mass difference of the U-tube, with and without the tar. The yields of char, tar and gas, termed  $Y_{\text{char}}$ ,  $Y_{\text{tar}}$  and  $Y_{\text{gas}}$ , are determined from  $W_{\text{char}}$  and  $W_{\text{tar}}$  by Eqs. (1), (2) and (3), respectively. Three experiments were performed at each condition, and the relative standard deviation of  $Y_{\text{tar}}$  is about 4.3%.

$$Y_{\text{tar}} = W_{\text{tar}}/W_{\text{coal,daf}} \times 100\% \quad (1)$$

$$Y_{\text{char}} = W_{\text{char}}/W_{\text{coal,daf}} \times 100\% \quad (2)$$

$$Y_{\text{gas}} = 100\% - Y_{\text{tar}} - Y_{\text{char}} \quad (3)$$

### 2.2. Reaction of tar

The reaction of tar was performed in glass tubes of 2 mm in inner diameter and 30 mm in length. Each of the glass tube was charged with  $7 \pm 0.05$  mg tar, purged with nitrogen for 1 min, and then sealed by a blast burner. The glass tubes were inserted in holes of a preheated copper block, which allows fast heating of the samples while prevents overheating. After a certain time the glass tubes were taken out of the heating block and cooled quickly in air, and then installed directly in an electron spin resonance (ESR, A200 Bruker) unit for radical measurement. It should be noted that the lifetime of radicals varies greatly. The radicals that survive in nanoseconds can't be detected by ESR. However, due to poor mobility or inaccessibility by steric hindrance, some radicals have long lifetime and those can be detected by ESR [1,20]. The ESR was operated at 9.76 GHz and 1.578 mW. The central magnetic field was 3484 G, the modulation amplitude was 1.0 G, the sweep width was 100 G, the sweep time was 0.35 min, and the time constant was 0.04 s. The measurements were carried out at  $25$  °C, and the signals were calibrated by 2,2-diphenyl-1-picrylhydrazyl (DPPH). The radical concentration in tar ( $R_{\text{tar}}$ ) is calculated by Eq. (4), where  $N_{\text{R}}$  is the amount (mol) of radicals in tar, and  $m_{\text{tar},0}$  is the mass (g) of tar initially in the glass tubes. Three experiments were performed under each

Table 1  
Proximate and ultimate analyses of the coal.

Proximate analysis (wt.%)			Ultimate analysis (wt.%, daf)				
Mad	Aad	Vdaf	C	H	O <sup>a</sup>	N	S
6.4	7.1	37.9	81.8	4.3	12.2	1.2	0.5

ad: air-dry basis; daf: dry-and-ash-free basis.

<sup>a</sup> By difference.

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