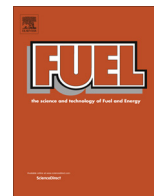




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Behaviors of radical fragments in tar generated from pyrolysis of 4 coals

Q1 Wenjing He^a, Zhenyu Liu^{a,*}, Qingya Liu^{a,c,*}, Donghui Ci^b, Caroline Lievens^b, Xiaofen Guo^b^a State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China^b Coal Upgrading Center, National Institute of Clean-and-Low-Carbon Energy, Beijing 102209, China^c Department of Chemistry, Northwestern University, Evanston, IL 60208, USA

HIGHLIGHTS

- Coal pyrolysis tars contain radicals at a level of 10^{16} spins/g.
- Coal tars generate more radicals and coke at temperature of 573 K or higher.
- The coke formed in the coal tars contains radicals at a level of 10^{19} spins/g.
- The coke formation in the tars follows the 2nd order kinetics with E_a of 200 kJ/mol.
- The coal tars are relatively more stable than biomass tars.

ARTICLE INFO

Article history:

Received 7 February 2014

Received in revised form 8 May 2014

Accepted 21 May 2014

Available online xxx

Keywords:

Coal
Pyrolysis
Tar
Radicals
Reactivity

ABSTRACT

Fast pyrolysis, with high heating rates and short retention time, was studied extensively in past decades due to high liquid yields. Although many fast pyrolysis processes have been developed and tested, few were reported to be successful on commercial scale due to problems including poor tar quality and system plugging. It is, therefore, important to exam the reactivity of the fast pyrolysis tars particularly at temperatures they may experience upon releasing from the coal surface. Four coals of different ranks were pyrolyzed to study the reactivity of the tars. It is found that the tars contain high concentrations of radicals and are highly reactive at temperatures higher than 623 K to generate more radicals and form coke. The coke formed in the tars contributes most of the radicals in the tar samples. The coking behavior can be expressed by the second order kinetics with activation energies of around 200 kJ/mol. The coal tar's reactivity is significantly less than that of biomass tars obtained from the same pyrolysis reactor under the same conditions.

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1. Introduction

Pyrolysis of coal has been applied on large scales to produce coke, tars (oil and chemicals), and coke oven gas for more than a century. Successful technologies are those characterized by slow heating rates and long pyrolysis time although they were believed to result in low tar yields. To increase tar yields, fast pyrolysis with heating rates in a range of $10\text{--}10^4$ K/s and reaction time in seconds has been studied in past decades worldwide [1–3]. The aim of the fast heating and fast cooling was to avoid the secondary reactions, such as retrogressive or condensation reactions, as much as

possible because they were considered to be the main reasons for the low tar yields [4–6]. Many fast pyrolysis processes have been developed and tested with this understanding but few were reported to be successful on commercial scale. The main problems of these fast pyrolysis processes were poor oil quality and severe system plugging due to deposition of cement-like materials in the product lines [7–9]. The failing of extensive efforts in reactor modification and product separation in solving these problems indicates that new insight should be gained to solve the problems especially on the fundamental chemistry involved.

It is well recognized that pyrolysis of coals follows a radical mechanism [10], starting with thermal cleavage of covalent bonds to generate volatile radical fragments and following by coupling of the radical fragments to form stable products [11–14]. Many works have tried to monitor radicals in coal pyrolysis and to correlate them with pyrolysis conditions [15,16], however, most of them focused on radicals in the solids (the raw feeds and the char) with limited attention on radicals in the tars [17]. Since the coupling of

* Corresponding authors. Address: Box 35, Beijing University of Chemical Technology, China. Tel.: +86 10 64421073; fax: +86 10 64421077 (Z. Liu). Address: Department of Chemistry, Northwestern University, Evanston, IL, 60208 USA, Tel.: +1 847 491 2982 (Q. Liu).

E-mail addresses: liuzy@mail.buct.edu.cn (Z. Liu), qingya.liu@northwestern.edu (Q. Liu).

radicals is governed by the probability of the radicals to get close to each other, fast pyrolysis may reduce the extent of the coupling reactions in the reactor and consequently result in more radicals in the tars and more radical reactions in the product lines [18,19], which are closely related to the poor quality and stability of the tars and plugging of the product lines.

In this work, we show radical concentration of tars obtained from pyrolysis of four coals in a temperature range from room temperature to 813 K, and report detailed changes in radical concentration of the tars heat treated at various temperatures to study the reactivity of the tars. The temperatures are those the tars would experience in large scale reactors and pyrolysis systems upon their release from the coal surface, including the high temperature product lines or the volatile/solid separation units, or in the heating units of tar refining. Kinetics of the coke formation in the tars under these high temperature conditions is also studied.

2. Experimental

The four coals studied are Hulunbeier coal (HLBE), Bulianta coal (BLT), Buertai coal (BET) and Daliuta coal (DLT), all from China. The coals were ground to sizes of 100–140 mesh and dried at 383 K in a vacuum for 4 h. The proximate and ultimate analyses of the coals were determined and shown in Table 1.

The details of pyrolysis experiments, electron spin resonance (ESR) tests, and heat treatment of the tars have been described elsewhere [20]. Briefly, the pyrolysis experiments were carried out in a tubular reactor, shown in Fig. 1, under a flow of N₂ at 200 mL/min with a heating rate of 80 K/min and a final temperature of 813 K. The residence time of the volatiles is about 3 s in the furnace zone before being condensed into tar. The tar was sampled by a capillary of 1 mm in diameter and then weighed, sealed in a glass tube suitable for the ESR test, and then stored in liquid nitrogen. The char was cooled to room temperature in N₂, sampled into the capillary and weighed, and then sealed in the glass tube suitable for the ESR test. All the ESR tests were carried out at room temperature, and the temperatures of the samples were controlled at room temperature during the test. The capillary and the glass tube showed little influence on ESR measurement. To simulate the high temperature environment the tars would experience, upon their release from the coal surface, in a large scale reactor or pyrolysis systems, the tars (sealed in glass tubes) were subjected to a heat treatment, i.e. kept in a heating jacket maintained at 293, 373, 473, 573, 623, 673, 723 or 773 K for 4 h. The radical concentrations of the tars kept at these temperatures were tested at 0.5, 1, 2, 3 and 4 h of the heat treatment. The tar samples were then extracted by tetrahydrofuran (THF) for 12 h after the glass tubes been cut open at the two ends. The THF insoluble matters staying in the capillaries, termed coke, were quantified after being dried at 348 K in a vacuum for 4 h. The coke yield, defined as the mass of the coke divided by the mass of tar sample in percentage, were determined. The radical concentrations of the coke staying in the capillaries were also determined by ESR.

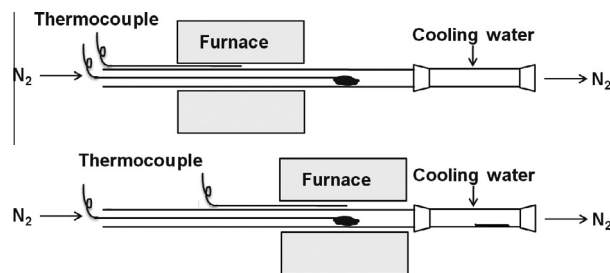


Fig. 1. The schematic diagram of the pyrolysis apparatus.

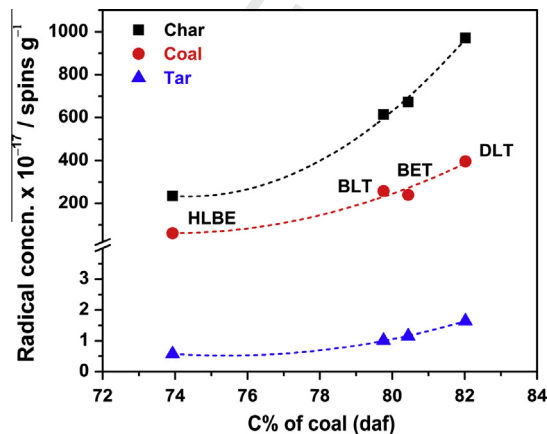


Fig. 2. Radical concentrations of the four coals and their pyrolysis products.

3. Results and discussion

3.1. Radical concentrations of the coals and the pyrolysis products

Fig. 2 shows the radical concentrations of the four coals and their pyrolysis products, tars and chars. It is clear that the radical concentrations of the coals, chars, and tars all increase with an increase in coal rank, namely the C% of the coals. The radical concentrations of the coals are about 10¹⁸–10¹⁹ spins/g, which agree well with that reported by Retcofsky for American coals [21]. The radical concentrations of the chars are in the level of 10¹⁹ spins/g, which are higher than that of the corresponding coals. The radical concentrations of the tars are in a level of 10¹⁷ spins/g, which are much lower than that of the coals and the chars.

In principle and in the simplest case, the thermal cleavage of a covalent bond in coal may generate two radical fragments, which are both volatiles or one of them is volatile while another one is non-volatile. If contact between the non-volatile and the volatile radical fragments is limited, one would expect that the radical concentration of the char is higher than that of the coal. This is the case shown in Fig. 2. This estimation also indicates that the number of

Table 1
Proximate and ultimate analysis of the raw materials.

Raw materials	Proximate analysis (wt.%)				Ultimate analysis (wt.%, daf)				
	Coal	Symbol	M _{ad}	A _{ad}	V _{ad}	C	H	O ^a	N
Hulunbeier	HLBE	30.99	9.10	29.94	73.93	5.12	19.43	1.14	0.38
Bulianta	BLT	13.04	12.34	30.55	79.76	4.85	13.92	1.06	0.40
Buertai	BET	5.13	14.77	31.11	80.44	4.77	13.57	1.02	0.20
Daliuta	DLT	4.89	6.11	28.97	82.02	4.58	11.90	0.92	0.59

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

^a By difference.

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