



## Full Length Article

# The radical and bond cleavage behaviors of 14 coals during pyrolysis with 9,10-dihydrophenanthrene



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## HIGHLIGHTS

- The stable and active radicals generated in pyrolysis of 14 coals are quantified.
- The coals contain unconvertible radicals that are likely to be in fusinite.
- The amounts of bonds cleaved in coal pyrolysis decrease with increasing coal rank.
- The radicals generated in pyrolysis are 3 order of magnitude more than that in coal.
- The bonds cleavage in coal pyrolysis with DHP follows the 1st order kinetics.

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## ABSTRACT

The pyrolysis of 14 coals with carbon contents (C%) of 67.5–94.9% are studied in the presence of 9,10-dihydrophenanthrene (DHP) at 440 °C. The amounts of stable radicals in the coals and that generated in the pyrolysis are quantified by electron spin resonance (ESR). The amounts of active radicals generated in the pyrolysis are quantified by the amounts of hydrogen donated by DHP. The changes in quantity of these radicals during the pyrolysis are correlated with the parameters representing the coal rank (C%, the amounts of aromatic and aliphatic carbon). It is found that the quantity of stable radicals of the coals in the pyrolysis increases with an increase in C%. The lignites and bituminous coals break up significantly in the first 2 min in the pyrolysis. All the coals contain some rigid structures that do not break at 440 °C and the structure can be categorized to fusinite. The quantities of active radicals generated in the pyrolysis are approximately 3 orders of magnitude higher than that of the stable radicals in the coals. The total amounts of cleavable bonds in the coals and the rate constants of the bond cleavage are determined by the first order kinetics.

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## 1. Introduction

Pyrolysis is an important step in many coal conversion processes [1]. Although it is well recognized that pyrolysis of coals involves two primary reactions, i.e. the decomposition of coal macromolecules to generate primary volatile products and the reaction of the primary volatile products to yield final products, researches and knowledge on coal pyrolysis focused mainly on the yield and composition of final products [2,3]. This dissatisfaction was attributed by many to the complex nature of coals in

structure and in composition. The understanding of coal pyrolysis mechanism is still a subject that needs to be studied.

The coal pyrolysis mechanism can also be described more fundamentally from the point of view of radicals. It is because that all the coals contain radicals [4] and the pyrolysis of coals starts with thermal cleavage of weak covalent bonds to generate radical fragments that is followed by reaction of volatile radical fragments to yield final products, such as gas, tar and coke [5,6]. Because a coal contains various types of covalent bonds of different dissociation energies [5], these two radical reactions occur not only sequentially but also concurrently in coal pyrolysis. Furthermore, the products of the second reaction may undergo further pyrolysis to yield additional radical fragments. In addition, the radical fragments may not be fully coupled through the second reaction and

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may remain in the final products, typically in coke and tar. These remained radicals were ascribed, at least partially, to the problems encountered in downstream processing of tar, such as increasing in viscosity, solidification during storage, transport and separation [7], as well as cracking and coking during preheating for refining. Clearly, it is very important to thoroughly understand the mechanism of radical generation and radical reaction, and the relationship between these radical behaviors and the covalent bonds in coals.

To study the radical mechanism of coal pyrolysis, it is necessary to determine the radical concentrations in coal and in the pyrolysis products, especially during coal pyrolysis under various conditions. ESR has been used in-situ or ex-situ to measure radicals in coals and in coal pyrolysis products, which yields quantitative and qualitative results. The works that have been carried out include those on behavior of total radicals [8,9] and those on kinetic models [10,11]. However, because most of the radical reactions are too faster to be measured by ESR [12], ESR data show only stable radicals that are either poor in mobility or confined in rigid structures that constitutes steric hindrance to other radicals [7,13]. Therefore, many researchers doubted about the ESR's capability in monitoring the active radicals.

Studies have shown that the radicals generated in coal pyrolysis in the presence of hydrogen donor solvents (typically the partially hydrogenated aromatics, 9,10-dihydrophenanthrene (DHP), for example) can be coupled or stabilized by acquiring hydrogen from the solvents, during which the solvents convert to the corresponding aromatics [14,15]. This indicates that in the presence of a sufficient amount of a hydrogen donor solvent the majority of the active radicals generated in coal pyrolysis can be coupled by hydrogen from the donor solvent, which minimizes the coupling of coal radicals and allows determination of the quantity of active radicals by the amount of aromatics formed from the donor solvent. This method has been applied recently to a study of biomass pyrolysis [16], which showed that more than 99.9% of the radicals generated in the pyrolysis of lignin, cellulose and hemicellulose at temperatures of 350, 400 and 440 °C acquired hydrogen from DHP at a DHP to biomass mass ratio of 8 while the stable radicals measured by ESR accounted only less than 0.1% of the total radicals.

To determine the quantities of the active and stable radicals in pyrolysis, and to correlate the changes in these radicals with coal rank, the behaviors of these radicals in pyrolysis of 14 coals in the presence of a sufficient amount of DHP were studied at 440 °C in this work. The relations between behaviors of the radicals and the properties of coals are studied, and a kinetic model is developed to show the relations.

## 2. Experimental

### 2.1. Materials

A series of coal samples varying from lignite to anthracite are used, and their ultimate and proximate analyses are shown in Table 1. XLT and SL are lignites. YL, YZ, ZZ, AUC, QLS and LA are bituminous coals. RQG, QS, JC, TX and SH are anthracites. The coals were ground to pass 100 mesh sieve, and dried under a vacuum at 110 °C for 24 h. The hydrogen donor solvent DHP was purchased from Tokyo Chemical Industry Co., Ltd. and was used as received.

### 2.2. Pyrolysis experiments

The pyrolysis experiments were performed in glass-tube-reactors with 2 mm inside diameter and 38 mm length under a nitrogen atmosphere. Each of the reactors was charged with 2 mg coal and 0–16 mg DHP and then purged with nitrogen for

**Table 1**

The ultimate and proximate analyses of the coal samples.

Sample name	Sample code	Proximate analysis (wt%)			Ultimate analysis (daf, wt%)				
		M <sub>ad</sub>	A <sub>d</sub>	V <sub>daf</sub>	C	H	O <sup>a</sup>	N	S
Xiaolongtan	XLT	14.0	16.1	47.8	67.5	4.1	24.1	1.9	2.4
Shengli	SL	15.0	13.4	47.8	67.7	4.5	25.7	1.3	0.8
Daliuta	DLT	4.9	13.2	42.9	72.4	4.5	20.6	1.5	1.0
Yilan	YL	5.4	2.6	44.0	73.8	5.0	19.5	1.4	0.3
Yanzhou	YZ	2.1	12.0	42.6	76.7	5.2	12.5	1.5	4.1
Zaozhuang	ZZ	0.4	8.9	34.5	83.7	5.2	8.7	1.6	0.8
AU coking	AUC	0.2	8.4	23.0	85.9	4.7	7.2	1.7	0.5
Qinglongshan	QLS	0.5	10.1	17.8	88.6	4.4	5.0	1.4	0.6
Luan	LA	0.4	12.2	13.9	88.8	4.2	4.9	1.7	0.4
Ruqigou	RQG	0.5	15.3	10.1	90.3	3.2	5.3	1.0	0.2
Qinshui	QS	0.8	12.0	7.3	91.0	3.1	4.4	1.1	0.4
Jingcheng	JC	1.5	29.0	7.5	91.4	2.9	4.4	0.9	0.4
Taixi	TX	1.1	2.5	6.8	91.9	2.1	5	0.9	0.1
Sihe	SH	0.8	8.2	6.0	92.1	3.1	3.3	1.1	0.4

M: moisture; A: ash; V: volatile; ad: air dry; d: dry; daf: dry-ash-free.

<sup>a</sup> By difference.

1 min before being sealed by a blast burner. Each of the reactors was then inserted into a quartz tube immersed in a fluidized sand bath maintained at 440 °C. The time required to heat the sample to 440 °C is less than 0.25 min. The quartz tube was removed from the sand bath at the designated time and quenched quickly in a water bath and then stored in liquid nitrogen.

### 2.3. ESR measurements

The free radical concentration of a sample was measured at 18 °C by installing the glass-tube reactor directly in a Bruker EMXplus-10/12 ESR spectrometer operated at 9.85 GHz and 0.1 mW. The central magnetic field was 348 mT, the modulation amplitude was 1.0 G, the sweep width was 5 mT, the sweep time was 50 s and the time constant was 0.01 s. The signals were calibrated by 2,2-diphenyl-1-picrylhydrazyl (DPPH). The ESR signal intensity and radical concentration showed excellent linearity, and the reactor itself showed no ESR signal. No radical was detected in blank experiments (with DHP but without the coals). The amount of free radicals in a sample detected by ESR ( $R_D$ ) is calculated by Eq. (1):

$$R_D = N_R/m_{daf} \quad (1)$$

where  $N_R$  is the amount (mol) of radicals in the sample and  $m_{daf}$  is the mass (g) of coal on the dry-ash-free basis. The relative deviation of  $R_D$  estimated by parallel experiment is less than 10%.

### 2.4. Determination of the amount of hydrogen donated by DHP

The amounts of DHP and its reaction products were determined by a high performance liquid chromatograph (HPLC) as reported previously [16]. DHP can donate hydrogen to radicals from coals by converting itself to phenanthrene (PHE). PHE may also form from disproportion and ring-opening reactions of DHP [16] but its amount is low (less than 4.7%) and can be determined by the amounts of 1,2,3,4-tetrahydrophenanthrene (THP) and 2-ethylbiphenyl (EBP) as reported previously [16]. Therefore, the amount of hydrogen donated to coal radicals,  $R_H$ , is determined by Eq. (2) on the daf coal basis:

$$R_H = 2(N_P - N_{THP} - N_{EPB})/m_{daf} \quad (2)$$

where  $N_P$ ,  $N_{THP}$  and  $N_{EPB}$  are the amounts (mol) of PHE, THP and EPB determined by the HPLC analysis, respectively. The relative deviation of  $R_H$  estimated by parallel experiment is less than 4%.

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