



Research article

Behavior of radicals during solvent extraction of three low rank bituminous coals



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ABSTRACT

Solvent extraction of coals has been practiced extensively for various purposes including the determination of coal structure. It is generally assumed that the extraction is mainly a physical process involving little change in covalent bonds. But different opinions were reported. This work studies the behavior of radicals during extraction of 3 low rank bituminous coals using 5 solvents, including hexane, toluene, tetrahydrofuran (THF), 1,2,3,4-tetrahydronaphthalene (THN), and *N*-methyl-2-pyrrolidinone (NMP), using electron spin resonance (ESR). The extractions are carried out at temperatures from the ambient temperature to temperatures somewhat higher than the boiling points of the solvents, as well as under ultrasound. It is found that the radical concentration of the coals changes during the extraction, and the change is influenced by temperature and varies with the solvent. The decrease in radical concentration in most solvents at temperatures lower than their boiling points is attributed to coupling of free radicals dissolved from the coals, while the increase in radical concentration at high temperatures and in NMP is attributed to the cleavage of weak bonds in coals by the solvents.

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1. Introduction

It is generally recognized that the organic portion of coals is a collection of macromolecules linked together by inter-molecular forces that are weaker than covalent bonds. Literatures showed that some of the macromolecules in coals were extractable by solvents, and the quantities of extractants vary greatly, depending on the types of coals as well as the types of solvents.

Iino et al. showed that the yields of extractants of Shin-yubari coals (86 wt.% carbon, daf) at the ambient temperature were 9.3 wt.% in *N*-methyl-2-pyrrolidinone (NMP) but 55.3 wt.% in a mixture of solvents containing CS₂ and NMP (CS₂-NMP) at a volume ratio of 1. The yield of extractants increases with increasing coal rank, from 4.6 wt.% of lignite to 65.6 wt.% of mid-rank bituminous coals in CS₂-NMP [1]. These behaviors were also demonstrated by Wei et al. [2].

It is generally believed that the solvent extraction of coals at milder conditions dissociates only the inter-molecular bonds that are weaker than covalent bonds [3,4], and the molecules that dissolved in solvents do not react with each other [5,6], so the extractants were widely used to study the structure of coals.

Literatures also showed that coals contain large amounts of radicals and their radical concentration increases with increasing coal rank, from 5×10^{18} spins/g of lignite to 5×10^{19} spins/g of anthracite [7–9], for

example. Different from the free radicals that are reactive because they move freely and couple quickly in nanoseconds, the radicals in coals are stable because they are confined in the solid structure and are inaccessible to other radicals [10–11]. It was reported that radicals present in both of the extraction residues and extractants [4,12], suggesting that the radicals in extractants may react with each other due to increased mobility in solvents [13,14]. However, the researches carried out to explore this behavior showed different results. Seehra studied NMP extraction of Bakerstown coal (79.6 wt.% carbon, daf) at the ambient temperature and reported that the overall quantity of radicals did not change during the extraction, although the radical concentration of extraction residue is higher than that of the coal while the radical concentration of extractants is lower than that of the coal [6]. Seehra further pyrolyzed the coal and its NMP extractant and residue in a temperature range of 400–600 °C and reported that the quantity of radicals in the pyrolyzed “coal” were similar to the weighted average of radicals of the extractant and residue pyrolyzed at the same temperature [6]. Fowler et al. studied chloroform extraction of Linby coal (83.0 wt.% carbon, daf) by Soxhlet extraction and compared the radical concentrations of coal with that of the extraction residue, before and after pyrolysis under the same conditions [15]. They reported similar results as that of Seehra, i.e. the solvent extraction does not involve radical reactions.

Duber et al. [13], Takanohashi et al. [14] and Doetschman et al. [16], however, reported results different from the above. Duber et al. studied ethylenediamine (EtDA), pyridine (Py) and tetrahydrofuran (THF) extraction of a coal from the mine Jankowice in Upper Silesia (80.7 wt.%

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Table 1
Proximate and ultimate analyses of the coals.

Sample	Proximate analysis (wt.%)			Ultimate analysis (wt.%, daf)				
	M_{ad}	A_{ad}	V_{ad}	C	H	O ^a	N	S
BLT	13.1	12.3	30.6	79.8	4.9	13.8	1.1	0.4
BET	5.1	14.8	31.1	80.4	4.8	13.6	1.0	0.2
DLT	4.9	6.1	29.0	82.0	4.6	11.9	0.9	0.6

M: moisture; A: ash; V: volatile matter; *ad*: air dry; *daf*: dry-and-ash-free basis; a: by difference.

carbon, daf), and found that at the ambient temperature the radical concentrations of extractants were lower than that of the extraction residues, and that of the extraction residues were lower than that of the coal. The overall change in the extraction was approximately 30% reduction in quantity of radicals, which was attributed to coupling of radicals dissolved in the solvents [13]. Doetschman et al. extracted 8 coals with carbon contents of 74.0–91.8 wt.% (daf) at the ambient temperature by a CS₂-NMP (1:1 in volume) solution. They also found reduction in radical's quantity during the extraction and attributed the behavior to coupling of radicals dissolved in the solvent [16]. Takanohashi et al. extracted 5 coals with carbon contents of 76.9–86.2 wt.% (daf) by the CS₂-NMP (1:1 in volume) solution and found that the radical concentration of the extractants were lower than that of coals, which were lower than that of extraction residues. The weighted total radical concentrations of extractants and residues decreased for coals with carbon contents of 76.9 and 79.4 wt.% but increased for coals with carbon contents of 82.0, 82.6, and 86.2 wt.% [14].

Based on the above discussion, it is certain that the radical behavior of coals during solvent extraction is complex and has not been well understood. It is possible that the complication is partially resulted from the effect of extraction temperature, which was found to play a role in radical concentration by Fowler [15]. Furthermore it is very possible that the methods used in separating extractants from residue affected the radical concentration data, because removing solvent from extractants was usually accomplished by solvent evaporation at temperatures as high as 150 °C, which may induce reaction of some radicals. It is also possible that some of the solvents used cannot be fully removed from the extractants as well as from the extraction residues even at high temperatures [17], which increased errors in determination of radical concentrations [18]. The environments, especially those containing oxygen, used in drying the extractants and extraction residues may also affect the radical concentration of the samples [15].

Increasing temperature and applying ultrasound have been found to be effective to promote solvent extraction processes [19–21]. Li et al. studied extraction of Banko coal by NMP, hexahydroanthracene, and their mixtures at temperatures of 60–260 °C. They found increase in radical concentration with increasing extraction temperature especially when NMP was the solvent [19]. Matturro et al. extracted three coals (lignite, subbituminous, and bituminous) with a solvent mixture composed of pyridine, *n*-Bu₄NOH, and CH₃OH. They found that the extraction yields of the coals ranged from 65 to 77 wt.% in the presence of ultrasound, which were much higher than those in the absence of ultrasound, 27–29 wt.% [21]. However, little research was reported on changes in radical concentration during these processes.

Table 2
The physical property data of the solvents.

Compound	Boiling point (°C)	Polarity	Dielectric constant (F/m) [34]	Viscosity (mPa·s) [34]
Hexane	68.7	0.06	1.89 (20 °C)	0.31 (25 °C)
Toluene	110.6	2.4	2.28 (20 °C)	0.59 (20 °C)
THF	66	4.2	7.6 (20 °C)	0.55 (20 °C)
THN	207.2	–	2.73 (20 °C)	2.02 (20 °C)
NMP	203	10.2 (≈water [32])	32.0 (25 °C)	1.65 (20 °C)

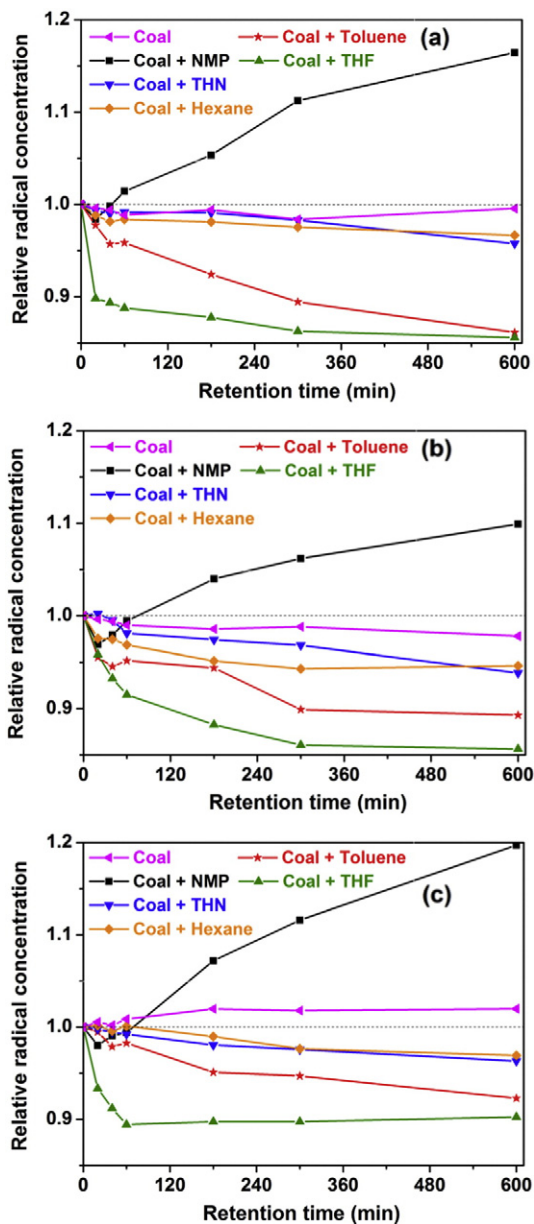


Fig. 1. Radical concentration of “coal + solvent” for BLT coal (a), BET coal (b), and DLT coal (c).

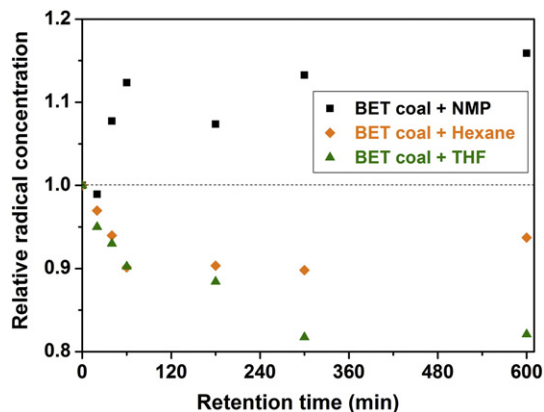


Fig. 2. Radical concentration of residues derived from extraction of BET coal by 3 solvents.

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