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Fractionation of coal by use of high temperature solvent extraction technique and characterization of the fractions

Ryuichi Ashida, Kyosuke Nakgawa, Masayuki Oga, Hiroyuki Nakagawa, Kouichi Miura *

Department of Chemical Engineering, Kyoto University, Kyoto 615-8510, Japan

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Abstract

The authors have recently presented a new coal fractionation method that can separate a bituminous coal into several fractions, just like petroleum distillation, without decomposing coal. In this paper this method was applied to two bituminous coals and a brown coal. Sequential solvent extraction at different temperatures lower than 350 °C successfully separated the two bituminous coals into several fractions having different molecular mass compounds. Since all the extracted fractions are almost free from mineral matter, and some fractions were found to be fusible like a synthesized pitch when heated, the possibility of producing high performance carbon materials from the coal fractions was investigated. On the other hand, fractions obtained from the brown coal by the sequential solvent extraction were very close in both chemical composition and molecular mass, although the sequential extraction could greatly suppress the decomposition of the brown coal below 350 °C. The difference in the extraction behavior between the bituminous coals and the brown coal were attributed to the difference in their chemical structure.

Keywords: Coal fractionation; Solvent extraction; Carbon materials

1. Introduction

Coals have been mainly used as energy resource through their combustion or gasification, while petroleum has been utilized not only as energy resource but also as sources of chemicals. It is probably because, while chemicals can easily be recovered from liquid petroleum through distillation process, it has been very difficult to isolate valuable compounds from the solid coal. It may therefore be a key to develop a coal separation method corresponding to the refinery process of petroleum for the effective utilization of coals in the future.

The authors have recently succeeded in fractionating a bituminous coal [1,2] by utilizing the solvent extraction method that we proposed [3–6]. The proposed solvent extraction method extracts coal using a flowing stream of non-polar solvent such as tetralin or 1-methylnaphthalene under 10 MPa at temperatures lower than 350 °C. The fractionation can be realized through sequential extraction at different temperatures. The bituminous coal (a strongly-caking coal) was separated into several fractions having different molecular mass, just like petroleum distillation, without decomposition.

There have been several studies on solvent extraction of coal. Since they have been performed mostly for investigating the structure of coal, it was necessary for them to increase the extraction yield. For this purpose, they used strong polar solvents such as pyridine [7], and/or binary solvents such as CS_2-NMP [8]. In our extraction method, on the other hand, thermal energy below 350 °C was utilized to release the aggregate structure of coal molecules instead of using such strong solvents. The released molecules can be dissolved even in a non-polar solvent such as 1-methylnaphthalene or tetralin because the solubility of the coal molecules in the non-polar solvent is well enhanced at high temperature. This concept is advantageous for a practical process of coal fractionation being proposed by

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* Corresponding author. Tel.: +81 75 383 2663; fax: +81 75 383 2653.
E-mail address: miura@cheme.kyoto-u.ac.jp (K. Miura).

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the authors because strong interaction between coal and strong solvents makes it difficult to separate the solvent from the coal.

In this study the proposed method was applied to fractionate three different rank coals: two bituminous coals having different caking properties and a brown coal. Then the fractions obtained were characterized in detail to examine if the proposed method can fractionate different ranks of coals. The possibility of utilizing the fractions as raw materials for high performance carbon materials was also investigated.

2. Experimental

2.1. Coal samples

Two bituminous coals, Gregory coal (GR) from Australia and Witbank coal (WT) from South Africa, and an Australian brown coal, Loy Yang coal (LY), were used in this study. GR is a strongly-caking coal, whereas WT is a slightly-caking coal. The properties of the coals are given in Table 1.

2.2. Experimental procedure of coal fractionation

The procedure of the proposed extraction method has been described in detail in the previous papers [1–6]. The non-polar tetralin was used as the solvent. It is well known that tetralin acts as a hydrogen donor at as high as 350 °C. So, we have compared the extraction performance using tetralin and 1-methylnaphthanele, and we found that both solvents gave almost the same extraction yield below 350 °C for several coals. Then we decided to use tetralin, because 1-methylnaphthalene is too expensive. The coal fractionation started from the extraction at 150 °C as shown in Fig. 1. This extraction separated coal into the residue, the solid extract that precipitated from the extract at room temperature (deposit), and the extract soluble in solvent even at room temperature (soluble). The deposit obtained by this extraction is a fraction which precipitated as solid at 25 °C from the extract obtained at 150 °C. This means that the deposit is soluble at 150 °C but becomes insoluble in tetralin at between 25 °C and 150 °C. From this viewpoint, the deposit obtained by the 150 °C extraction is represented as "Frac.+25–150". Then the residue and the soluble obtained by the 150 °C extraction are, respectively, referred to as "Frac.+150" and "Frac.−25" here.

Next, the Frac.+150 was subjected to the extraction at 200 °C, which fractionated the Frac.+150 into Frac.+150–200 and Frac.+200. This extraction procedure was repeated sequentially by raising extraction temperature by 50 °C up to 350 °C. Fig. 1 shows that five sequential extraction steps can fractionate a coal into eight fractions in principle. All the fractions except Frac.−25 were obtained as solid. The Frac.−25, which was still soluble in tetralin at room temperature, was mixed with an excessive amount of *n*-hexane to precipitate a part of it as solid. The solid precipitated by this operation was called "TS-HI" and the fraction which was soluble in *n*-hexane was called "HS" hereafter.

2.3. Analyses of fractionated coals

The fractions obtained were characterized through various analyses. The laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOFMS; Shimadzu/

Table 1
Ultimate analyses of coal samples used and their fractionated coals

Sample	Ultimate analysis (wt%, d.a.f.)				Atomic ratio (–)		Ash (wt%, d.b.)
	C	H	N	O (diff.)	H/C	O/C	
Gregory (GR)							
Raw coal	83.9	5.4	1.2	9.5	0.77	0.08	6.4
Frac.−25 (TS-HI)	85.3	5.9	1.5	7.3	0.82	0.06	0.3
Frac.+200–250	84.8	5.6	1.8	7.8	0.79	0.07	0.2
Frac.+250–300	84.8	5.4	1.7	8.1	0.76	0.07	0.5
Frac.+300–350	84.5	5.6	1.8	8.1	0.78	0.07	0.7
Frac.+350	84.0	5.3	1.5	9.2	0.75	0.08	12.3
Witbank (WT)							
Raw coal	81.0	5.1	2.0	11.9	0.75	0.11	9.6
Frac.−25 (TS-HI)	84.1	6.3	1.8	7.8	0.89	0.07	0.3
Frac.+200–250	81.5	5.6	2.6	10.3	0.82	0.09	1.1
Frac.+250–300	82.3	5.6	2.5	9.6	0.81	0.09	1.1
Frac.+300–350	82.5	5.7	2.4	9.4	0.82	0.09	0.9
Frac.+350	82.8	4.9	1.9	10.4	0.71	0.09	11.5
Loy Yang (LY)							
Raw coal	66.9	4.7	0.7	27.7	0.84	0.31	1.5
Frac.−25 (TS-HI)	77.9	6.4	0.5	15.2	0.98	0.15	0.7
Frac.+250–300	73.0	6.0	0.7	20.3	0.98	0.21	1.6
Frac.+300–350	76.1	5.6	0.7	17.6	0.88	0.17	1.6
Frac.+350	75.7	4.6	0.8	18.9	0.72	0.19	2.5

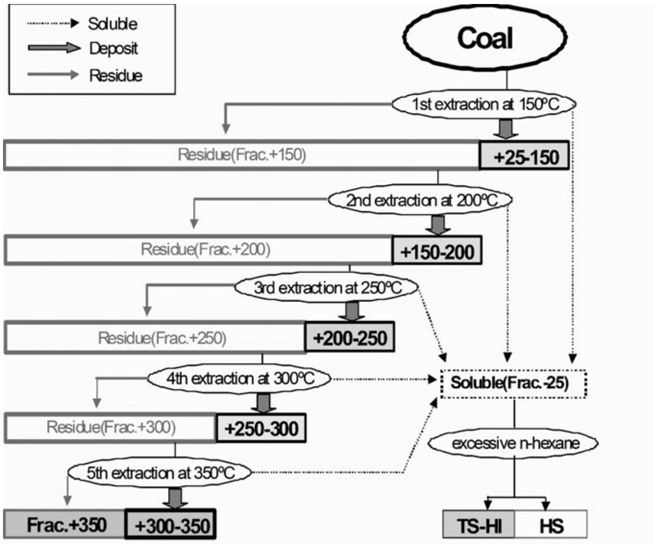

Fig. 1. Scheme of coal fractionation by solvent extraction.