Multistep extraction of coal

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Unlike many natural and synthesized polymers, coal is a mixture of polyfunctional high-molecular-mass material. The usually observed limited extractability of coal is attributed to the disregard of various relatively strong intra- and intermolecular interactions and their co-operativity. Due to the polyfunctionality, ionic, charge-transfer and so-called π–π interactions are present, and their abundances are highly rank-dependent. Such relatively strong interactions are not completely solvated in a single step with any solvent. In this paper, multistep extraction was studied to solvate these interactions. Pyridine was mostly used after treatments to disrupt these interactions without breaking covalent bonds. Much larger pyridine extractability was obtained compared to a single step extraction. As solubilization or extraction is the first step to characterize coal, caution is advised against the limited extractability obtained by conventional procedures.

(Keywords: coal; extraction; pyridine)

There is a long history, over a century, of coal–solvent extraction. Only a small fraction of most coals is extractable with organic solvents; the average amount being 20–30 wt%. In order to explain this, hydrogen bonds have been primarily considered in addition to weak van der Waals' forces[1,2], and these were assumed to be broken with one of the best solvents, pyridine. Caution, however, is advised against the limited extractability of coal, because solubilization of various relatively strong intra- and intermolecular (secondary) interactions caused by polyfunctional groups in coal have not been fully considered.

The overlapping $2p_z$ orbitals on each sp^2-hybridized carbon between polycyclic aromatic compounds (PAC) generate an electron cloud over and under the planner PAC molecules, as reviewed by Haenel and Schweitzer[3]. Electronically excited complexes are formed by the so-called π–π interaction. The relatively strong π–π interaction in higher rank coal has been recently pointed out[4–6]. However, other kinds of relatively strong secondary interactions in lower rank coals have been poorly understood. A charge-transfer interaction has been proposed to be a relatively strong secondary force in high-volatile bituminous coal and to bring about the solvent-induced association[7,8]. Although there are indications of the presence of the ionic force in lower rank coal[9,10], the effect of the ionic force on solvent extractability has not been thoroughly reported. The significant effect of the ionic force on pyridine extractability has been recently observed for lower rank coal by Nishioka *et al.*[8].

These relatively strong ionic, charge-transfer and π–π interactions are present in addition to hydrogen bonds and weak van der Waals' forces. These are not completely overcome with pyridine. Any single solvent cannot solvate all of these secondary interactions. The abundances of diverse functional groups in coal are highly rank-dependent, and the strength and importance of individual interactions change according to rank. So, each interaction has to be solvated step by step using different procedures according to coal rank.

Macromolecules with relatively strong intra- and intermolecular interactions co-operatively interact[11]. This co-operativity is presumably significant in coal and makes solubilization of coal difficult. Unfortunately, the co-operativity of coal with polyfunctionality has been ignored.

Therefore, solubilization of coal must be very difficult by a single step with any solvent. Solubilization or extraction of macromolecules is the first step for their characterization, but limited values of extractability have been used to characterize coal. Extraction of coal by a single step with single solvents has been introduced from procedures generally used for other polymeric material. Unlike many natural and synthesized polymers, coal is a mixture of polyfunctional high-molecular-mass material. Another extraction procedure appropriate for coal needs to be explored.

In this paper, multistep extraction is studied as a method of extracting solubles from coal; it will be a series of extractions using different solvents, or extractions with a selected good solvent after a series of treatments to disrupt various secondary interactions without cleaving covalent bonds. In this study, pyridine is mostly used after treatments. The objective is not to make many attempts or to search for optimum extraction procedures, but to demonstrate how to approach multistep extractions of coal.

EXPERIMENTAL

American Chemical Society reagents and h.p.l.c.-grade solvents were used. Tetrahydrofuran (THF) was distilled before use, and the other solvents were used without

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