

# Strong interactions between selected compounds and coal

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Interactions between coal and a coal liquid and also between coal and various standard compounds were investigated. The mixtures were soaked in cyclohexane under nitrogen at 25, 200 and 350°C for 2 h, and recoveries of the coal liquid and standard compounds were determined by solvent extraction. Nearly 100% of neutral compounds were recovered after the treatment. However, weakly acidic aromatics containing a hydroxyl group and basic aromatics containing nitrogen were selectively adsorbed on coal even at 25°C, and complete recovery with tetrahydrofuran and pyridine was difficult. The adsorption of weakly acidic compounds was stronger than that of basic compounds. The adsorption became stronger when the mixtures were soaked at higher temperatures. Similar results were also observed for the coal liquid.

(Keywords: selected compounds; coal; strong interactions)

It is known that pyridine is retained in both extract and residue after Soxhlet extraction of coal<sup>1-5</sup>. Pyridine is not completely removed from these materials even after drying under high vacuum at ~100°C. The amount of pyridine retained reaches 1–10 wt%. As retained pyridine is easily exchangeable with free pyridine<sup>1</sup>, this is physical incorporation in coal.

Maleic anhydride is incorporated in high-volatile bituminous coal by heating at 100–200°C in solvents such as benzene and chlorobenzene<sup>6-8</sup>. A portion of the maleic anhydride incorporated is the adduct of the Diels–Alder reaction, but a significant amount of unreacted maleic anhydride is physically retained<sup>9</sup>. Although maleic anhydride is easily dissolved in water and methanol, it is difficult to recover the adsorbed maleic anhydride with these solvents.

It is known that hydrogen bonds are major interactions in coals of lower rank<sup>10-12</sup>. Compounds containing functional groups such as –OH and –NH– interact with coal through hydrogen bonds. As it is estimated that most of the hydrogen bonds can be broken with pyridine<sup>13,14</sup>, such compounds would be readily recovered with pyridine. However, if interactions between coal and such compounds are relatively strong, these compounds may not completely be recovered with pyridine. The charge-transfer interaction is one of the important relatively strong interactions in high-volatile bituminous coal<sup>15</sup>. Some portions of charge-transfer complexes in the coal cannot be solvated with pyridine<sup>15</sup>, although pyridine is a good electron-donor solvent. Charge-transfer complexes in the original coal are readily broken at higher temperature, and more stable charge-transfer complexes are formed. Therefore the strength and abundance of selective interactions or complexes in coal may change at higher temperature.

These results show that coal interacts strongly with selected compounds. However, interactions between selected molecules and coal have not been fully studied.

Understanding this selective interaction is important to investigate intra- and intermolecular interactions in coal and also from the practical point of view of coal utilization. Coal is mixed with solvents and oils in many processes such as liquefaction and combustion. Selective molecular interactions may occur in such processes. Compounds in a recycle oil may be selectively adsorbed on coal, and have a considerable effect on liquefaction. If compounds are selectively adsorbed on coal in combustion of a mixture of heavy oil and coal, they may change the efficiency of combustion.

In this paper, selective interactions in high-volatile bituminous coal were studied by using various types of standard compounds and a coal liquid. Mixtures of standards and coal and of a coal liquid and coal were soaked at three different temperatures, and the recoveries of the components were determined.

## EXPERIMENTAL

Illinois No. 6 coal (DECS-2, <850 µm) was obtained from the DOE Coal Sample Bank at Pennsylvania State University. Its elemental analysis was (wt%, dry): ash, 16.2; C, 65.5; H, 4.6; N, 1.1; S, 4.5. A 10 g sample was Soxhlet-extracted with pyridine for 72 h, Soxhlet-rinsed with methanol for 24 h, and dried under vacuum at 95°C overnight; the residue (PI) was also used in the study. A coal liquid derived from Illinois No. 6 coal in the Wilsonville pilot plant<sup>16</sup> was used. HPLC-grade solvents were used. Tetrahydrofuran (THF) was distilled before use; the other reagents were used without purification.

Coal samples (5 g) were charged into a 250 ml autoclave, and 10 ml of coal liquid and 50 ml of cyclohexane were added. The autoclave was evacuated and purged with nitrogen five times, and then heated at 5 K min<sup>-1</sup> to 200 and 350°C under nitrogen (initial pressure 0.35 MPa). The mixtures were heated at 200 or 350°C for 2 h while being agitated with the autoclave stirrer (500 rev min<sup>-1</sup>). For the treatment at room temperature, the mixtures were agitated under nitrogen

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