Solvent swelling behaviour of Shenmu-Fugu and Shengli coals

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Abstract: Swelling behaviors of Shenmu-Fugu bituminous coal (SFBC) and Shengli lignite (SLL) in various organic solvents were investigated at temperatures ranging from 0 °C to 55 °C. The results show that tetrahydrofuran (THF) has a relatively higher swelling ratio in comparison to other solvents, suggesting that THF likely disrupts coal-coal cross-links between macromolecular network structures in coal. SLL swelled more highly than SFBC in methanol (MA), indicating that MA interacts strongly with specific sites on SLL. Swelling ratios of SFBC in carbon disulfide (CDS), recycle liquefaction solvent (RLS) and initial liquefaction solvent (ILS) are appreciably higher than those of SLL. Coal swelling increases with raising temperature within the temperature range studied (0-55 °C), especially in polar solvent.

1. Introduction

Solvent swelling is a widely used, convenient and low-cost method for understanding the nature of fossil fuels with cross-linked macromolecular network structures. Solvent swelling has been extensively used to determine solubility parameters [1], to characterize solvent-macromolecule interactions [2], for calculating the average molecular weight between cross-links, the cross-link density, and the number of repeat units per cross-link of macromolecular network structures [3-5]. The covalent cross-links and the noncovalent interactions of coal-solvent and coal-coal are two important factors in determining the extent of swelling [6-8]. In addition, swelling ratio is closely related to coal rank [8,9], swelling time [10], solvent type [11-13], and temperature [14]. Understanding the relationships is helpful for optimizing coal conversion processes, especially coal hydroliquefaction (CHL).

Solvent swelling of coal is a complex process. Numerous previous attempts have been made to better understand the swelling behaviour of coal [8,14-18]. A set of nonpolar solvents (cyclohexane, n-hexane, benzene, ethylenediamine, and carbon disulfide), polar solvents (pyridine, N-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF), butylamine, and hexylamine), and binary mixtures (pyridine-water, pyridine-toluene, pyridine-cyclohexane) have been used in these studies.

Hu et al. [19] investigated the effect of solvent swelling on the extraction of Xinglong coal. The results show that swelling pretreatment of coal with THF or pyridine can significantly enhance conversion and light-fraction yield of supercritical extraction process. Recently, direct coal liquefaction in the world, both on research and industrialization, has become a hot issue, and has been pushed to the peak of interest, especially for China which is a rapid developing country with limited petroleum resources.
reserves [20]. Although a large amount of work has been done, CHL is not yet competitive economically due to its harsh reaction condition and huge equipment investment. A variety of attempts, e.g., pre-swelling of coal [21] and the use of highly active catalysts [22,23], have been made to better develop economically feasible processes for CHL. Swelling is considered to be a critical process to determine coal reactivity for a liquid-solid mixture or a slurry system [11], such as CHL. Shenmu-Fugu bituminous coal (SFBC) and Shengli lignite (SLL) are of high quality being low in ash content, and extremely low in sulphur and suitable for direct liquefaction. Understanding swelling behavior of SFBC and SLL under different conditions is a subject for optimization of mild and directional CHL process. The aim of this investigation was to compare the solvent swelling behavior of SFBC and SLL in various organic solvents at different temperatures in order to provide a scientific basis for future sustainable development and industrialization of CHL.

2. Experimental

2.1. Coal sample and solvents
Recycle liquefaction solvent (RLS), initial liquefaction solvent (ILS), SFBC and SLL were provided by Beijing Research Institute of Coal Chemistry, China Coal Research Institute. Coal samples were pulverized to 200 mesh sieve and then dried in a vacuum at 80 °C for 24 h. Table 1 shows the proximate and ultimate analyses of the dried samples. Solvents carbon disulfide (CDS), methanol (MA), acetone (AT) and THF are commercially purchased analytical-pure reagents and were distilled prior to use.

### Table 1. Proximate and ultimate analyses (wt%) of SFBC and SLL.

| Sample | Proximate analysis | Ultimate analysis (wt %, daf) |
|--------|--------------------|-------------------------------|
|        | M_{ad} | A_{d} | V_{daf} | C   | H   | N   | S   | O_{diff} |
| SFBC   | 5.33   | 6.32  | 30.74   | 79.82 | 4.73 | 1.05 | 0.50 | 13.90 |
| SLL    | 20.41  | 19.00 | 45.99   | 72.20 | 4.95 | 0.30 | 1.10 | 21.45 |

2.2. Swelling procedure
About 3 g of the coal samples were placed in constant diameter glass tubes (5 mm i.d., ca. 120 mm length) and centrifuged in a Hitachi CR 22E centrifuge at 7500 r/min for 5 min and then the initial sample layer height (h_{i}) was measured. Solvent was then added to the tube followed by ultrasonic irradiation in a JY92-IIID ultrasonic tub for a prescribed period of time at indicated temperature. Then, the tube was centrifuged again as above, and the final sample layer height (h_{f}) was measured. The volumetric swelling ratio is equal to the ratio of h_{f} to h_{i}. The amount of solvent added was determined to ensure that the height of the solvent surface is a little higher than that of the coal surface.

3. Results and discussion

3.1. Effects of time and solvent
As Table 2 shows, the swelling of SFBC reaches equilibrium within 2 min in MA, 3 min in THF and CDS and 4 min in RLS and ILS. Equilibrium swelling ratio in different solvents decrease in the order: THF (2.00) >> CDS (1.33) > MA (1.24) > RLS (1.19) > ILS (1.14). The equilibrium swelling of SLL needs 3 min in AT, 4 min in MA, CDS and THF, 5 min in RLS and ILS, as exhibited in Table 2 and Figure 1. We obtained swelling ratio values of 1.65, 1.33, 1.24, 1.09, 1.04, and 1.03 in THF, MA, AT, CDS, RLS, and ILS, respectively.

### Table 2. Equilibrium swelling time and swelling ratios of SFBC and SLL in various solvents at 35 °C.

| Sample | THF | CDS | MA | AT | RLS | ILS | THF | CDS | MA | AT | RLS | ILS |
|--------|-----|-----|----|----|-----|-----|-----|-----|----|----|-----|-----|
| SFBC   | 3   | 3   | 2  | /  | 4   | 4   | 2.00 | 1.33 | 1.24 | /  | 1.19 | 1.14 |
| SLL    | 4   | 4   | 4  | 3  | 5   | 5   | 1.65 | 1.09 | 1.33 | 1.24 | 1.04 | 1.03 |
THF and pyridine are commonly quite good swelling solvents for bituminous coals. Swelling ratio of SFBC in THF is drastically higher than that in other solvents and also higher than that of SLL, as exhibited in Figure 1. THF is specifically interacting solvent, meaning that it is able to dissociate specific interactions (particularly hydrogen-bonding) within the coal. In comparison to other solvents, the much greater efficacy of THF may be partly due to the greater electron donor strengths of THF, but may also be due to the greater affinity of THF for coal [24]. Wang et al. [25] suggested according to the type of THF adsorption isotherm that THF may break the original hydrogen-bond cross-links between macromolecular chains in coal.

Swelling of coal changes with coal rank and solvent type. As shown in Figure 1, swelling ratios of SFBC in CDS, RLS and ILS are appreciably higher than those of SLL. Swelling ratios of SLL in polar solvents are significantly higher than those in nonpolar solvents. Takanohashi et al. [12] investigated swelling of low-rank coals with various solvents at room temperature. The results show that low-rank coals swelled more highly than higher-rank (subbituminous coals and bituminous coals) coals in polar solvents. As Figure 1 exhibits, swelling ratio of SLL in MA is appreciably higher than that in CDS, whereas for SFBC, swelling ratio in MA is slightly lower than that in CDS. According to the results reported by Takanohashi et al. [12], swelling ratio of low-rank coals in MA is appreciably higher than those in CDS, which are consistent with our results. In general, low-rank coals contain larger amounts of polar groups, e.g., carboxyl and hydroxyl, to interact with solvent by forming hydrogen bonds, which play a very important role in determining the swelling of coal in polar solvents [8]. This may be the dominate reason that SFBC has lower swelling ratio values than SLL in MA. In addition, higher-rank coals except anthracites comprise of more aromatic rings (ARs), especially more condensed ARs. The strong interactions between CDS and the ARs may be an important reason for higher swelling ratio of SFBC in CDS than in MA by weakening π–π interactions between ARs in SFBC. Wang et al. [25] also expected that nonpolar swelling solvent adsorb on coals by π–π interactions with ARs. The low swelling of SLL in CDS can be attributed to the strong ionic forces. Chen et al. believe that coal swelling in nonpolar solvents is mainly controlled by coal-coal interactions and that ionic forces in lignite restrains swelling of coal [8].

Although RLS and ILS are factually used in CHL process, both of them are poor solvents for SFBC and SLL swelling under the experimental conditions. RLS and ILS mainly consist of aliphatic and aromatic hydrocarbons with much higher molecular weights than THF, CDS and MA, correspondingly making them have much higher viscosity (16.84 cp at 40 °C for ILS, 15.87 cp at 40 °C for RLS). The high viscosity may retard the solvent access into micropores in coal, so the swelling of coals in them is very negligible, especially for SLL. These facts indicate that the high viscosity of ILS and RLS have

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**Figure 1.** Time profiles of SFBC and SLL swelling in different solvents at 35 °C.

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significantly adverse effects on the higher conversion yield of CHL. Therefore how to improve swelling ratio of liquefaction coal in ILS and RLS is advantageous for the coal liquefaction process.

3.2. Effect of temperature
As Figure 2 exhibits, swelling ratio of SFBC appreciably increased with raising temperature and reach maximums at 35°C in RLS and at 45°C in other solvents. Noteworthily, swelling ratio of SFBC in both MA and ILS remarkably increased with raising temperature from 35 to 45°C so that swelling ratio of SFBC in ILS becomes the same as that in RLS at 45°C, but swelling ratio of SFBC in MA is still lower than that in CDS.

Swelling ratio of SLL in THF remarkably increased to ca. 1.71 from ca. 1.27 with raising temperature from 0 to 55°C, only slightly increased in MA and AT and almost no change in CDS, ILS and RLS, as illustrated in Figure 2.

Several researchers examined the swelling behavior of different coals in various organic solvents at various temperatures [26,27]. Their results show that the ultimate swelling ratios are independent of temperature within the temperature range studied and that the rates of swelling are increased. Otake et al. [14] also confirmed that there is no significant effect of temperature on the extent of swelling in the range from 10 to 60°C. But in the present experiments, we obtained the different results and noted swelling ratios of SFBC and SLL appreciably increased with raising temperature, especially in polar solvent. It is speculated that the rates of solvent diffusion increase with raising temperature. Increasing the temperature favors uptake of solvent by coal to strengthen the interactions of coal-solvent, especially for coal-polar solvent.

Figure 2. Temperature profiles of SFBC and SLL swelling in different solvents for 15 min.

4. Conclusions
The swelling of SFBC and SLL reach equilibrium within 5 min in various solvents. THF is quite good swelling solvents and RLS and ILS are very poor swelling solvents for SFBC and SLL. Swelling ratios of SFBC in CDS, RLS and ILS are appreciably higher than those of SLL. SLL has substantially higher swelling ratios in MA in comparison to SFBC. Swelling ratios of SFBC and SLL appreciably increased with raising temperature, especially in polar solvent.

Acknowledgments
This work was supported by the Key Research and Development Program (Social Development) of XuZhou (Grant KC18152) and a Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions.
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