석탄구조의 용매팽윤시 용매간 시너지효과

윤 용 승
고등기술연구원 전력에너지연구실

Synergistic Effects of Solvents on Coal Swelling

Yongseung Yun
Electric Power System Laboratory, Institute for Advanced Engineering

SUMMARY

Synergistic effects of mixed solvents, especially with mixtures of CS_2 with electron donor solvents, in inducing desired structural changes in coals were studied by solvent swelling techniques in addition to differential scanning calorimetric analyses. Mixed solvents exhibit significant synergistic efficacy in swelling the coal structure of medium bituminous rank. This synergy effect appears to be physical origin that is closely related to matching solubility parameters. Since the swollen coal structure can be obtained by mixed solvents with CS_2 at room temperature instead of high temperature, many possible technological pathways for economical utilization of coal might be sought.

INTRODUCTION

High-rank coals (> 86%C dry-ash-free basis (daf)) have been known to exhibit fundamentally different response characteristics to heat and solvent treatments than lower-rank coals (< 86%C daf). Sakurovs et al.[1] reported that heat is more effective than pyridine for creating mobility in coal structure, for coals of 86-90%C daf. Also Iino et al.[2] showed that extraction yields using solvent mixtures of CS_2/N-methyl-2-pyrrolidinone (NMP) (1:1 v/v) increase with carbon content up to 86%C daf and then fall rapidly with further increase in carbon content.

High-rank coals do not significantly swell in pyridine, while most lower-rank coals show a substancial amount of swelling in that solvent. However, some combinations of solvents, especially with CS_2, yield for the higher-rank coals similar swelling ratios as can be obtained in lower-rank coals. The work of Iino et al.[2-4] is especially noteworthy, since they first reported the benefit of mixing CS_2 (which is a known good solvent for fats, resins, and rubbers) to several solvents (i.e., pyridine, dimethylsulfoxide, dimethylformamide, dimethylacetoamide, NMP) in enhancing extraction yield and volumetric swelling of coal, particularly around 86 %C daf.

It has also been demonstrated that the structure of high-rank bituminous coals can be thermally loosened, to yield high volumetric swelling ratios in pyridine (when the coals are heated to above 350℃) [5]. These swelling ratios are similar to those which can be obtained at room temperature in mixtures of CS_2/pyridine, CS_2/dimethylsulfoxide, or CS_2/dimethylformamide as will be shown in this paper.

In order to understand the underlying structural changes caused by mixed solvents, as well as to explore possible effective pre-liquefaction strategies for these high-rank bituminous coals, coals were studied by solvent swelling techniques.

EXPERIMENTAL

Aliquots of two coal samples, viz., Upper Freeport medium volatile bituminous coal (-100 mesh) and Pocahontas No. 3 low volatile bituminous coal (-20 mesh) obtained from Argonne National Laboratory-Premium Coal Sample Program, were analyzed by Differential Scanning Calorimetry (DSC) and solvent swelling techniques. They were used as-received.

Solvent swelling

Coal samples were placed in constant diameter tubes (3 mm i.d., ca. 5 cm high) and centrifuged at 7500 rpm for 3 min in a roughly 30 cm horizontal rotor (SAVANT HSC-10K high speed centrifuge), after which the initial height of the sample was measured by a caliper. Solvent was then added and stirred until a visual check showed the total submergence of coal in solvent. The stirring was repeated frequently (normally 3 times) during the first 30 min following solvent addition. At the desired measurement times, the sample tubes were centrifuged again (7500 rpm for 3 min), the swollen coal height measured, and the solvent replaced with the clean solvent.

Sample Pretreatment

In order to determine the main parameters governing the relaxation of coal structure, several treatment were performed before subjecting the samples to solvent swelling. These include preswelling by solvent, pyridine Soxhlet extraction, acetylation, and heat treatment. Solvent preswelling was performed in two ways. Acetylation of hydroxyls was accomplished by mixing coal with excess pyridine and excess acetic anhydride at room temperature for about three days and then excess acetic anhydride was destroyed by reaction with water while excess pyridine was removed by washing the sample with water. The acetylated sample was subsequently dried under vacuum at room temperature for about two days.

RESULTS AND DISCUSSION

It has been noted [2-4] that higher rank bituminous coals show a remarkably high degree of extractability in mixtures of certain solvents with CS_2. The Upper Freeport coal shows a sharp increase in room temperature swellability in a mixture of pyridine and CS_2, as noted in Figure 1. There is no need to heat-treat the coal to achieve significant swellability, which suggests that a physical relaxation of the structure is all that is involved. There is, of course, the possibility that CS_2 undergoes chemical reaction with the coal, cleaving similar numbers of bonds as are cleaved during heat treatment, but there is no strong reason to believe that this should be so. Moreover, as the data of Figure 1 show, there is a maximum in swelling ratio for the 1:1 by volume mixture of pyridine and CS_2. It would be difficult to understand why, if CS_2 is a chemically reacting agent, such a stoichiometry would be needed, when solvent is in large excess. This led to the conclusion that the CS_2/pyridine mixtures are effective mainly because of specific solvent properties.

The fact that the CS_2/pyridine mixture relaxes the coal structure in a manner similar to heat, was reported earlier [5]. Treating the coal with CS_2 alone, pyridine alone, or chloroform/pyridine mixtures left intact the DSC peak, corresponding to the relaxation of the structure. The Upper Freeport coal treated in CS_2/pyridine, however, no longer showed such a relaxation event at 350°C. The CS_2/pyridine mixture was not nearly as effective a swelling agent for Pocahontas No. 3 coal as for Upper Freeport coal. This, too, was confirmed by the DSC which still recorded a significant relaxation event for the previously pyridine/CS_2-treated Pocahontas No. 3 coal. Apparently this specific solvent combination is only effective for a certain range of ranks. This is consistent with the observations of Iino et al.[3].

There is nothing particularly unique about the choice of pyridine in mixture with CS_2. As Iino et al. earlier showed [2,3], NMP/CS_2 mixtures are also effective. Results illustrated in Table 1 have established, as Iino et al. noted, that CS_2/dimethylsulfoxide(DMSO) and CS_2/dimethylformamide are also effective mixtures. Thus solvent pair needs not even to include a nitrogen base, since DMSO is not. All the effective solvents in CS_2 mixtures are, however, fairly good electron donors.

Pyridine was tried in admixture with other solvents of similar solubility parameter to CS_2, and with other solvents that could serve as effective electron acceptors (see Table 1). None of these other combination rivaled the ability of the CS_2/pyridine mixture to swell the Upper Freeport coal. Of course, these solvents did not yet include particularly strong electron acceptors (strong acids) which might be more effective for swelling.

Pretreatment of the coal by pyridine extraction has no effect on the conclusion (see Table 1). Pretreatment of the coal by acetylation does little to change the behavior of the coal with respect to swelling in CS_2/pyridine mixtures. This means that the structure is not irreversibly expanded to a significant extent by the acetylation alone. This suggests that it is not, for example, a xanthate formation type of process [6,7] involving CS_2 and the hydroxyl groups in the coal that results in the greater swellability of the coal in CS_2/pyridine mixtures.

Pretreatment of the coal in CS_2, followed by removal of the CS_2 by evaporation and then subjected to pyridine swelling, showed again the importance of the interaction of pyridine and CS_2. The sequence resulted in pyridine swelling comparable to that of the raw untreated coal (see Table 2). Reversing the order of sequential exposure was also not effective.

When the coal was relaxed by exposure to CS_2/pyridine mixtures, it was more swellable than in the raw state, by either of these solvents as shown in Table 2. The fact that the swellability was not as great as that induced by the thermal treatment to 350°C is also seen in Table 2. This is because once-swollen in pyridine/CS_2 mixture, it is difficult to fully remove all of the pyridine from the coal by vacuum drying. Thus the coal is already in a partially swollen state, due to the irreversibly bound pyridine. Heating a CS_2/pyridine swollen coal to 350°C results in a higher subsequent pyridine swellability (relative to the vacuum dried CS_2/pyridine swelled coal), because the pyridine is fully lost upon heating.

CONCLUSIONS

- Even strong solvents cannot swell the structure of high-rank bituminous coals more than ten percent at low temperatures (< 250°C) whereas heat treatment above 300°C under inert environment and solvent swelling by mixtures of solvents (e.g., with CS_2) enhance the swelling of coal structure significantly.
- The origin of efficacy in swelling by mixed solvents of CS_2 and certain

solvents (e.g., pyridine, dimethylsulfoxide, dimethylformamide) appears to be physical that is closely related to matching solubility parameter of coal with solvents and/or to adding solvents of high donor number.

REFERENCES

1. Sakurovs, R.; Lynch, L.J.; Barton, W.A. In *Coal Science II*; Schobert, H.H., Bartle, K.D., Lynch L.J., Ed.; ACS Symposium Series 461; ACS: Washington, D.C., 1991; Chapter 9, p. 111.
2. Iino, M.; Takanohashi, T.; Ohsuga, H.; Toda, K. *Fuel* **1988**, *67*, 1639.
3. Takanohashi, T.; Iino, M. *Energy Fuels* **1990**, *4*, 452.
4. Iino, M.; Matsuda, M. *Fuel* **1983**, *62*, 744.
5. Yun, Y.; Suuberg, E.M. *Fuel* **1993**, *72*, 1245.
6. Petrucci, R.H. *General Chemistry*; Macmillan Co.: New York, 1972.
7. Morrison, R.T.; Boyd, R.N. *Organic Chemistry*; Allyn and Bacon, Inc.: Boston, 1983.

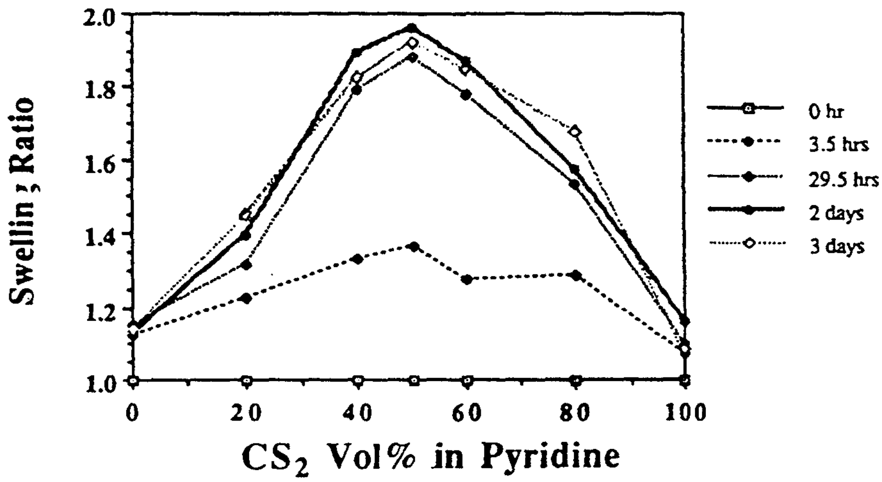

Figure 1. Changes of volumetric swelling ratio by mixed solvents of CS_2 and pyridine for Upper Freeport coal.

Table 1. Volumetric Swelling Ratio by Mixed Solvents (1:1 v/v) for Upper Freeport Medium Volatile Bituminous Coal

Pretreatment	Solvent mixture (1:1 v/v)	Solvent characteristics			Q**
		Solvent	Acceptor Number	δ (H)*	
None	CS_2/pyridine	pyridine	14.2	10.4	1.95
	CS_2/dimethylsulfoxide	dimethylsulfoxide	19.3	12.8	1.75
	CS_2/dimethylformamide	dimethylformamide	16.0	11.5	1.92
	CS_2/n-butylamine	n-butylamine	-	-	1.21
	pyridine/water	water	-	9.4	1.08
	pyridine/methanol	methanol	41.3	12.9	1.09
	pyridine/chlorobenzene	chlorobenzene	-	9.5	1.12
	pyridine/chloroform	chloroform	-	9.3	1.13
	pyridine/methylene chloride	methylene chloride	-	9.7	1.14
	pyridine/nitroethane	nitroethane	-	11.1	1.09
Pyridine Soxhlet extracted	CS_2/pyridine	CS_2	-	10.0	1.83
Acetylated	CS_2/pyridine	CS_2	-	10.0	1.71

*δ: solubility parameter in Hildebrand which is equivalent to $cal^{1/2}cm^{-3/2}$ **Q: volumetric swelling ratio

Table 2. Solvent Swelling Results for Upper Freeport Coal

Pretreatment	Solvent	Solvent Properties				Q*	Swelling number**
		Donor No.	Acceptor No.	δ(H)†	Molar Vol.(cc/mol)		($x10^3$)
None	pyridine	33.1	14.2	10.4	80.9	1.14	1.73
	CS_2	-	-	10.0	60.3	1.08	1.33
	n-butylamine	-	-	-	99.8	1.12	1.20
	THF	20.0	8.0	9.1	81.1	1.08	0.99
	dimethylsulfoxide	29.8	19.3	12.8	71.0	1.09	1.27
	dimethylformamide	26.6	16.0	11.5	77.4	1.08	1.03
CS_2 swelled	pyridine	33.1	14.2	10.4	80.9	1.12	1.48
Pyridine Soxhlet extracted	pyridine	33.1	14.2	10.4	80.9	1.19	2.35
	CS_2	-	-	10.0	60.3	1.07	1.16
CS_2/pyridine (1:1 v/v) swelled	pyridine	33.1	14.2	10.4	80.9	1.40	4.94
	CS_2	-	-	10.0	60.3	1.30	4.97
Heated under N_2 up to 350°C	THF	20.0	8.0	9.1	81.1	1.82	10.11
	pyridine	33.1	14.2	10.4	80.9	2.17	14.46
	CS_2	-	-	10.0	60.3	1.50	8.29
	dimethylsulfoxide	29.8	19.3	12.8	71.0	1.49	6.90
	chlorobenzene	-	-	9.5	101.7	1.40	3.93
CS_2/pyridine swelled and heated up to 350°C	pyridine	33.1	14.2	10.4	80.9	1.83	10.26
Acetylated	pyridine	33.1	14.2	10.4	80.9	1.10	1.24
	CS_2	-	-	10.0	60.3	1.06	0.99

†δ: solubility parameter in Hildebrand which is equivalent to $cal^{1/2}cm^{-3/2}$ *Q: volumetric swelling ratio **(Q-1)/molar volume