

HEAT TREATMENT OF COALS IN VARIOUS SOLVENTS AT TEMPERATURES AS LOW AS 175 - 300°C

Masashi Iino, Jianli Shen, Satoshi Ashida, Chunqi Li, and Toshimasa Takanohashi
Institute for Chemical Reaction Science, Tohoku University
Katahira, Aoba-ku, Sendai 980-77, JAPAN

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INTRODUCTION

Neavel (1) reported that more than 90% of a high-volatile bituminous coal became soluble in pyridine by coal liquefaction less than 5 min. at 400°C in tetralin. We are interested in the dissolution mechanism at this initial stage of coal liquefaction, since this stage seems to be a key step to control liquefaction yield and product selectivity. So, heat treatments of coals were carried out at temperatures as low as 175-300°C in various solvents which have different hydrogen donatability (2,3).

We are also interested in the mechanism of retrogressive reactions which concurrently occur with dissolution reactions in coal liquefaction. Although the details of retrogressive reactions are still obscure, hydrogen donation to coal fragments is essential for their suppression. Especially radicals formed during the initial stage of coal liquefaction must be stabilized to suppress efficiently the retrogressive reactions which could result in the formation of refractory, high-molecular weight substances. We have used carbon disulfide- N-methyl-2-pyrrolidinone (CS₂-NMP) mixed solvent (1:1 by volume) as an extraction solvent for the heat treated coals. The CS₂-NMP mixed solvent has been found to give high extraction yields (40-65wt%, daf) at room temperature for many bituminous coals (4). We also found that the extracts obtained with the mixed solvent include a considerable amount of the very heavy component which is not soluble in THF or pyridine, but soluble in the mixed solvent, i.e., heavier extract fraction than preasphaltene. (5).

In the previous study (2,3) the heat treatments of several bituminous coals such as Upper Freeport and Illinois No. 6 coals were carried out in solvents of different hydrogen-donatability under N₂ atmosphere. In tetralin retrogressive reaction was observed at 175-250°C and dissolution proceeded at 300-350°C. While in dihydroanthracene (DHA) or hexahydroanthracene (HHA), which have higher hydrogen-donatability than tetralin, the coals used underwent dissolution reactions even at low temperatures such as 175-250°C. The quantity of hydrogen transferred from the solvents to coals, which was estimated from dehydrogenation of the solvents such as anthracene from DHA, was found to be well correlated with the extent of the dissolution reactions occurred. However, recent study on the heat treatment of coals in NMP, which seems to have little hydrogen-donatability from its chemical structure, showed that for some coals NMP gave higher dissolution yields than HHA, the strongest hydrogen donor among the solvents we used.

In this study the heat treatments of coals in NMP at 175-300°C were carried out and the dissolution mechanism in NMP will be discussed, compared with that in HHA.

EXPERIMENTAL

The coals used in this study are shown in Table 1. NMP and HHA were used as a solvent for heat treatment of coals.

Heat treatment of the coal was performed in 50ml magnetically stirred autoclave at 175, 250, and 300°C, respectively. 1g of the coal and 5g of the solvent were charged into the autoclave, which was pressurized with nitrogen to 5.0 MPa at room temperature. After the heat treatment, the coal was fractionated into the CS₂-NMP mixed solvent-insoluble fraction (MI) and -soluble fraction (MS), and then MS further into tetrahydrofuran (THF) -insoluble, the mixed solvent soluble fraction (TIMS) and THF-soluble fraction (TS), with the mixed solvent and THF at room temperature under ultrasonic irradiation, as shown in Figure 1. The quantity of MI and TIMS was determined after drying overnight in vacuum at 80°C and that of TS was calculated by difference, i. e., 100-MI-TIMS. The dissolution yield was defined here as the sum of TIMS and TS.

RESULTS AND DISCUSSION

Heat treatment of coals in NMP and HHA

Figure 2 shows the fraction distribution after the heat treatment of Upper Freeport coal in NMP and HHA at 175°C, 250°C, and 300°C, together with the fraction distribution before the heat treatment, i. e., for the raw coal, which was obtained from the extraction of the raw coal with the CS₂-NMP mixed solvent and the fractionation of the extract obtained. At 175°C NMP gave higher dissolution yield (TIMS + TS) than HHA and little effect of temperature on the dissolution yield and fraction distribution was observed in NMP, unlike the case with HHA, suggesting different dissolution mechanisms for NMP and HHA. Figure 3 shows the result for Zao Zhuang coal and the similar tendency was obtained as Upper Freeport coal. Figure 4, 5 and 6 show the results for Pittsburgh No. 8, Illinois No. 6 and Beulah-Zap coals, respectively. The heat treatments of Pittsburgh No. 8 and Illinois No. 6 coals gave nearly 80% of the dissolution yields at 300°C, higher than those in HHA. Figure 7 shows the plot of net dissolution yields for the heat treatment of the coals in NMP and HHA at 300°C versus C% of the coals. The net dissolution yields here are the dissolution yield corrected for the yield for the raw coal, i. e., $(\text{TIMS} + \text{TS})_{300^\circ\text{C}} - (\text{TIMS} + \text{TS})_{\text{raw coal}}$. Figure 7 shows that for the low rank coals NMP gave higher net dissolution yields than HHA. Figure 8 shows radical concentrations of the raw Zao Zhuang coal and after the heat treatment for 1h at 300°C in HHA (a) and NMP (b). This clearly shows that in HHA the radical concentrations decrease as the increase of the heat treatment temperature, but in NMP the reverse tendency was obtained. As described in INTRODUCTION, hydrogen transfer from HHA to the coals was observed and it was well correlated with the dissolution yields. However, in the heat treatment in NMP no dehydrogenated derivatives of NMP was detected, indicating no hydrogen transfer from NMP to the coals.

Dissolution Mechanism in NMP and HHA

It is clear from the results described above that the dissolution reactions in NMP and HHA proceed through different mechanisms. In HHA coal radicals, which formed by the scission of very weak covalent bonds at 175-300°C and/or indigenous radicals activated by heat at these temperatures, may be responsible for the dissolution. These radicals are stabilized by the hydrogen donation from HHA and the dissolution reactions proceed. When the heat treatment was carried out in tetralin at 175 and 250°C, which is a much poorer hydrogen donor than HHA and hardly donate hydrogen to the radicals at these low temperatures, retrogressive reactions such as the addition to aromatic rings and coupling reactions occur.

The dissolution mechanism in NMP is not clear, though it is sure that hydrogen transfer from NMP to the coals does not occur. NMP is a polar solvent and a better solvent for coal extraction than pyridine, especially for low-rank coals which have many polar groups. One tentative explanation is that NMP dissolves much of coal molecules and radicals at 175-300°C and prevent retrogressive reactions which would occur in a non-polar solvent. Ionic reactions is also conceivable in NMP, though we have no evidence for it now.

Finally, it should be noted that the results above described were obtained by the use of the CS₂-NMP mixed solvent as an extraction solvent for the reaction mixture. If THF is used as a starting extraction solvent instead of the mixed solvent, we can only see small change of TS in the heat treatments carried out here.

CONCLUSIONS

Heat treatments of 7 coals were carried out in HHA which is a strong hydrogen donor, and in NMP which is a strong extraction solvent for coals, at temperatures as low as 175-300°C. HHA and NMP gave high dissolution yields for high- and low-rank coals, respectively. Hydrogen donation from HHA to coal radicals and high solubility for coal molecules and radicals are suggested to be responsible for these dissolutions.

REFERENCES

1. Nieveel, R. C. *Fuel*, **1976**, *55*, 237-242.
2. Shen, J., Takanohashi, T., and Iino, M. *Energy Fuels*, **1992**, *6*, 854-858.
3. Shen, J., and Iino, M. *Energy Fuels*, **1994**, *8*, 978-983.
4. Iino, M., Takanohashi, T., Osuga, H., and Toda, K. *Fuel*, **1988**, *67*, 1639-1647.
5. Iino, M., Takanohashi, T., Obara, S., Tsueta, H., and Sanokawa, Y. *Fuel*, **1989**, *68*, 1588-1593.

Table 1 Ultimate and ash analyses of coals

Coal	Ultimate analysis (wt%,daf ^b)					Ash (wt%,db ^c)
	C	H	N	S	O ^a	
Pocahontas No.3 (PC)	89.7	4.5	1.1	0.7	4.0	4.8
Zao Zhuang (ZZ)	86.9	5.1	1.5	1.6	4.9	7.4
Upper Freeport (UF)	86.2	5.1	1.9	2.2	4.6	13.1
Pittsburgh No.8 (PB)	82.6	5.5	2.1	2.4	7.4	8.7
Illinois No.6 (IL)	76.9	5.5	1.9	5.6	10.1	10.4
Wyoming (Wy)	75.1	5.5	1.1	0.4	17.9	5.2
Beulah-Zap (BZ)	71.6	4.8	1.0	0.9	21.7	9.6

^a By difference

^b Dry ash free basis

^c Dry basis

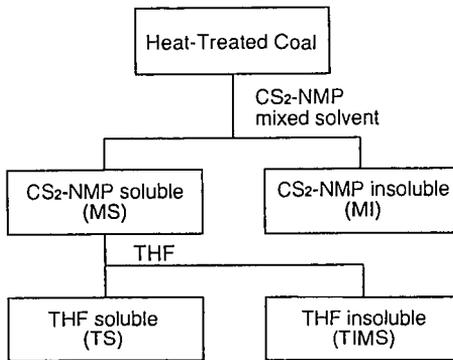


Figure 1 Extraction and fractionation procedures for the heat treated coals

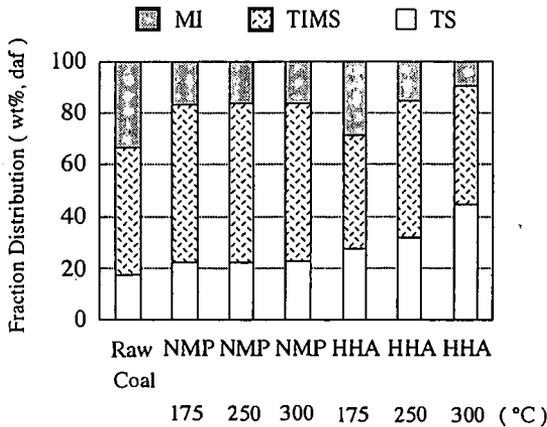


Figure 2 Fraction distribution after the heat treatment of Upper Freeport coal at 175-300°C in NMP and HHA for 1h, together with that for the raw coal.

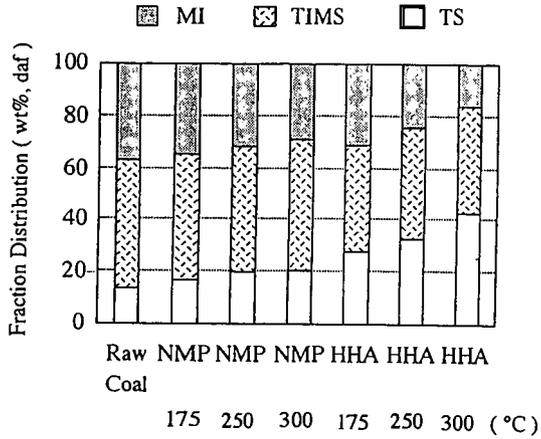


Figure 3 Fraction distribution after the heat treatment of Zao Zhuang coal at 175-300°C in NMP and HHA for 1h, together with that for the raw coal.

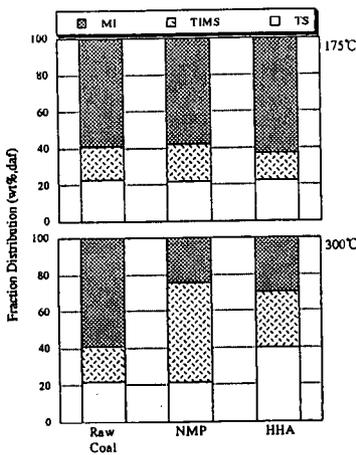


Figure 4 Fraction distribution after the heat treatment of Pittsburgh No. 8 coal at 175 and 300°C in NMP and HHA for 1h, together with that for the raw coal.

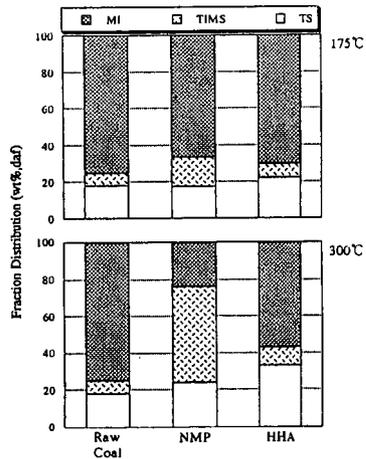


Figure 5 Fraction distribution after the heat treatment of Illinois No. 6 coal at 175 and 300°C in NMP and HHA for 1h, together with that for the raw coal.

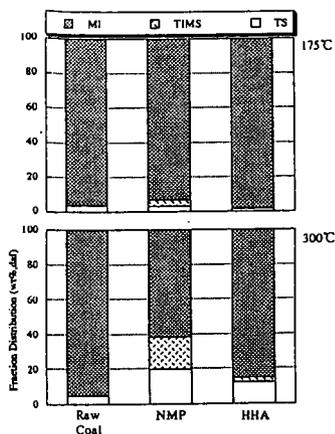


Figure 6 Fraction distribution after the heat treatment of Beulah-Zap coal at 175 and 300°C in NMP and HHA for 1h, together with that for the raw coal.

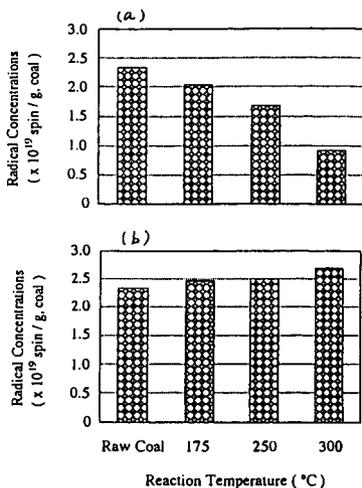


Figure 8 Radical concentrations of the raw Zao Zhuang coal and after the heat treatment for 1h at 300°C in HHA (a) and NMP (b).

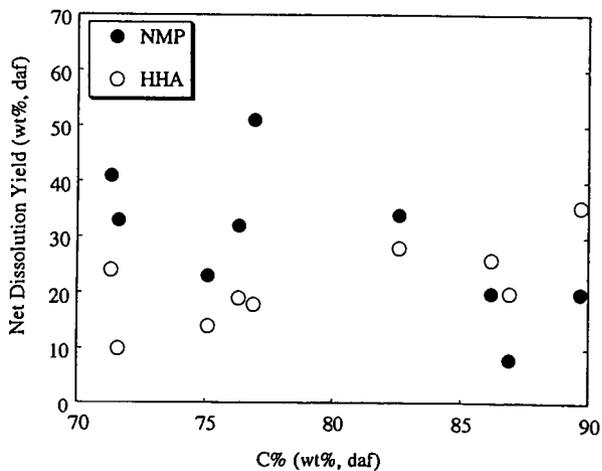


Figure 7 Plot of net dissolution yields for the heat treatment of the coals in NMP (●) and HHA (○) for 1h at 300°C versus C% of the coals.