

# HYDROGEN TRANSFER BETWEEN COAL AND TRITIATED ORGANIC SOLVENT

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## INTRODUCTION

To develop coal conversion techniques into useful fuels and chemicals by thermolysis and hydrogenation, it is important to elucidate the coal structure.<sup>1,2)</sup> Although coal has a complex structure which includes various aromatics and functional groups, it can be considered that the reactivities of hydrogen in coal could reflect the coal structure since each hydrogen in aromatics, aliphatics, functional groups with heteroatoms etc. has the different reactivities. Therefore, the determination of reactivities of hydrogen in coal will provide significant information for coal structure.

Useful methods to measure hydrogen in coal are to utilize isotopes such as deuterium and tritium tracers.<sup>3-11)</sup> A deuterium tracer was effective to trace reactive sites in coal and coal model compounds, however, there were few examples which enable quantitative analysis of the hydrogen mobility in coal because of the poor solubility of coal products and the difficulty of quantification of the deuterium tracer.<sup>3-7)</sup> In contrast, we have reported that tritium tracer techniques were effective to trace quantitatively hydrogen in the coal liquefaction.<sup>8-11)</sup> In these works, it was shown that the quantitative analysis of hydrogen transfer in coal could be given through the hydrogen exchange reactions among coal, gas phase and solvent as well as hydrogen addition. However, the method under coal liquefaction conditions includes destruction of the original structure of coal. In the course of our study, we were interested in the direct non-destructive determination of hydrogen in coal with its original form. Recently, we have reported that the tritium tracer methods are effective to determine the amount of hydrogen in the functional group of coal and examine the reactivities of hydrogen in coal through the reaction of coal with tritiated water and gaseous hydrogen in a pulse flow reactor or a batch reactor.<sup>12-14)</sup>

In this study, we investigate the hydrogen transfer between coal and tritiated organic solvent to estimate the reactivity of hydrogen in coal. A hydrogen donor solvent tetralin was tritiated with tritiated water. To avoid significant destruction of the coal structure, reaction was performed in the range 200-300 °C below usual coal liquefaction conditions. After the reaction of coal with tritiated tetralin, the reaction of the tritiated coal and water was carried out to remove tritium in functional groups and to obtain the information for the position of hydrogen exchanged in coal.

## EXPERIMENTAL

### Reaction of Coal with Tritiated Tetralin

Four kinds of Argonne Premium Coal Samples (Beulah-Zap (ND), Illinois No. 6 (IL), Upper Freeport (UF), and Pocahontas #3 (POC)) were obtained in 5 g of ampules (< 100 mesh). The samples of Wandoan coal (WA) were ground to -150 mesh particles. Coal samples were dried for 2 h at 110 °C under  $10^{-1}$  Torr. The analytical data of coals are shown in Table 1. Coal rank increases in the order ND < WA < IL < UF < POC and the oxygen content decreases in the same order. Tritiated tetralin was prepared by modifying the reported method.<sup>15)</sup> Tritiated water ( $2\text{g}, 10^8\text{ dpm/g}$ ), tetralin (1.2g), and sodium carbonate (0.005g) were added into a stainless tube reactor. After argon purge, the reactor was kept for 1 h at 420 °C under supercritical condition of water. After separation of tritiated water, tritiated tetralin was diluted to about  $10^6\text{ dpm/g}$  coal (0.5 g) and tritiated tetralin ( $0.5\text{ g}, 10^6\text{ dpm/g}$ ) was packed into a stainless tube reactor (6 mL). After the reactor was purged with argon, the reactions were performed under the conditions, 200-300 °C and 5-360 min. After the reaction, coal and tetralin were separated under vacuum at 200 °C for 2 h and the tritiated coal was washed with n-hexane, dried and oxidized by an automatic sample combustion system (Aloka ADS-113R) into tritiated water to measure its radioactivity. Every tetralin sample was dissolved into a scintillator solvent (Instafluor, Packard Japan Co. Ltd.) and measured with a liquid scintillation counter (Beckman LS 6500). The tetralin sample was also analyzed by gas chromatography equipped with FID

### Procedure of Hydrogen Exchange Reaction between Tritiated Coal and Water.

In order to predict locations of exchangeable hydrogen in coal, the hydrogen exchange reactions of coal that reacted with tritiated tetralin, i.e., tritiated coal, with water were performed. The tritiated coal and water were added into a glass reactor. The reactor was immersed into an oil bath with stirring. The reaction was performed at 100 °C for 24 h. After the reaction, suction filtration was performed and tritiated coal was washed with hot water. Further, the separated coal was dried under vacuum ( $< 10^{-1}$  Torr) at 120 °C for 1 h. After the coal was dried, it was oxidized by a method similar to the above using the combustion of coal.

### Calculation of Hydrogen Transfer Ratio.

Hydrogen transfer includes both hydrogen addition and hydrogen exchange. The Hydrogen Transfer Ratio (HTR) estimated in this paper means the ratio of the amount of hydrogen transferred into coal ( $H_{tr}$ ) to the total amount of hydrogen in an original coal ( $H_{coal}$ ). HTR between coal and tetralin was calculated on the basis of eq 1:

$$HTR = H_{tr} / H_{coal} \quad (1)$$

$H_{coal}$  was calculated with the analytical data presented in Table 1. The amount of hydrogen transferred from tetralin into coal ( $H_{tr}$ ) was calculated on the basis of eq 2:

$$R_{coal} / H_{tr} = R_{tet} / H_{tet}; \quad H_{tr} = H_{tet} \cdot R_{coal} / R_{tet} \quad (2)$$

$H_{tet}$  is the amount of hydrogen contained in tetralin and  $R_{tet}$  is the radioactivity of tritium contained in tetralin after the reaction. In eq 2, it was assumed that the hydrogen transfer reaction between tetralin and coal is at equilibrium. Thus after the reaction, the ratio of the radioactivity in coal to the amount of the hydrogen transferred in coal ( $R_{coal} / H_{tr}$ ) is equal to the ratio of the radioactivity in tetralin to the amount of hydrogen in tetralin after the reaction.

## RESULTS AND DISCUSSION

Figure 1 shows the change in hydrogen transfer ratio (HTR) of coal with reaction time at 300 °C. Total HTR increased with reaction time and reached constant value at 180 min. At this time, it can be considered that hydrogen transfer reaction has reached the equilibrium state. After hydrogen transfer reaction, the hydrogen exchange between the tritiated coal sample and water was performed to remove tritium in the functional group of coal and know the extent of hydrogen exchange of functional group in the reaction of coal with tritiated tetralin. As shown in Figure 1, HTR corresponding to the hydrogen exchange between hydrogen in functional group of coal and tetralin increased with reaction time similarly and reached the constant value at 180 min.

Figure 2 shows the change in HTR of coal with reaction temperature at 180 min. Although HTR was observed for each coal at 200 or 250 °C, this may be due to the sorption of tetralin molecule into coal as well as the hydrogen exchange. HTR remarkably increased in most of coals with increasing temperature from 250 °C to 300 °C, while HTR for POC coal increased only slightly. Total HTRs for all coals and HTRs corresponding to hydrogen exchange of hydrogen of functional group in coal with tritiated tetralin are listed in Table 2. The result shows that at lower temperature, 200 and 250 °C, hydrogen exchanges between hydrogen in functional group and tetralin were very low. These results were significantly different from those for the reaction of coal with tritiated gaseous hydrogen, where most of hydrogen in functional groups exchanged with tritiated gaseous hydrogen at the same lower temperature in the presence of catalyst.<sup>14)</sup> However, HTR for functional group of coal with tritiated tetralin also remarkably increased with a rise from 250 °C to 300 °C.

Figure 3 shows the change in tetralin conversion to naphthalene with temperature at 180 min. The trend of increase in tetralin conversion with temperature was similar to that in HTR. In the cases of lower rank coals, ND and WA, tetralin conversion increased with increasing temperature from 200 to 300 °C. In the cases of higher rank coals, IL, UF and POC, tetralin conversions were very low at temperatures 200 and 250 °C. However, those remarkably increased with a rise in temperature from 250 to 300 °C. The result suggests that, since lower rank coals, ND and WA, generated larger amount of radical species even at lower temperature, tetralin conversion

to naphthalene, that is hydrogen addition into coal was enhanced. For higher rank coals, however, it seems that a large amount of radicals were generated at 300 °C. Tetralin conversion for IL coal was highest at 300 °C and this may be due to the catalysis by a larger amount of pyrite included in IL coal.

In Figure 4, total HTR of coal with tritiated tetralin and HTR corresponding to hydrogen exchange for functional group in the reaction with tritiated tetralin at 300 °C and 360 min were compared with HTR corresponding to hydrogen exchange between coal and tritiated water at 100 °C which was previously reported. Except for ND coal, HTR corresponding to hydrogen exchange for functional group of coal in the reaction with tetralin was very similar to HTR of functional group between coal and tritiated water. The results shows that at 300 °C most of hydrogen in functional group of coal exchanged with tritiated tetralin. In the reaction of coal with tritiated tetralin, HTR decreased in the order IL>UF>WA>ND>POC which was different from that of the reaction of coal with tritiated water where HTR decreased with increasing coal rank.<sup>14</sup> There might be the decomposition of coal structure in lower rank coals at 300 °C which seems to affect the hydrogen transfer.

## CONCLUSIONS

Hydrogen transfer reaction between coal and tritiated tetralin significantly proceeded at 300 °C and the amount of hydrogen transferred increased in the order POC<ND<WA<UF<IL. The trend for temperature dependence of hydrogen transfer between coal and tetralin was very similar to that of tetralin conversion to naphthalene. Except for ND coal, most of hydrogen of functional group in coal exchanged with hydrogen in tetralin at 300 °C. In contrast, at lower temperatures, 200 and 250 °C, hydrogen transfer from tetralin to coal was very low for each coal and hydrogen in functional group only slightly exchanged.

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Table 1 Ultimate analysis of coals used (% daf)<sup>a)</sup>

Coal	C	H	N	S	O	
ND	72.94	4.83	1.15	0.70	20.38	(L)
WA	76.9	6.7	1.1	0.3	15.0	(SB)
IL	77.67	5.00	1.37	2.38	13.58	(HVB)
UF	85.50	4.70	1.55	0.74	7.51	(MVB)
POC	91.05	4.44	1.33	0.50	2.68	(LVB)

a) Abbreviations: ND: Beulah-Zap, WA: Wandoan, IL: Illinois No.6, UF: Upper Freeport, POC: Pocahontas No.3; L: lignite, SB: subbituminous coal, HVB: high-volatile bituminous coal, MVB: medium-volatile bituminous coal, LVB: low-volatile bituminous coal. Except for WA, samples are coals of the Argonne Premium Coal Sample Program.

Table 2 HTRs of coals with tritiated tetralin

Coal	200 °C		250 °C		300 °C	
	Total HTR	HTR of OH <sup>a)</sup>	Total HTR	HTR of OH <sup>a)</sup>	Total HTR	HTR of OH <sup>a)</sup>
ND	4.4	1.7	4.6	-	8.1	3.8
WA	2.5	0.3	3.3	1.0	9.0	4.6
IL	4.5	1.6	5.7	0.9	14.4	6.2
UF	2.8	1.4	3.5	-	11.7	2.0
POC	2.3	0.1	2.9	-	4.2	0.5

a) Hydrogen transfer ratio of functional groups such as hydroxyl group which was determined by the reaction of tritiated coal with water at 100 °C.

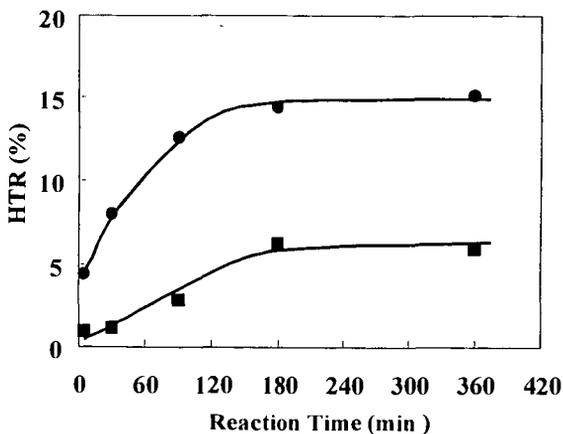


Figure 1. HTRs of Illinois No. 6 with [<sup>3</sup>H]tetralin at 300 °C  
 ●: Total HTR; ■: HTR for functional group in coal

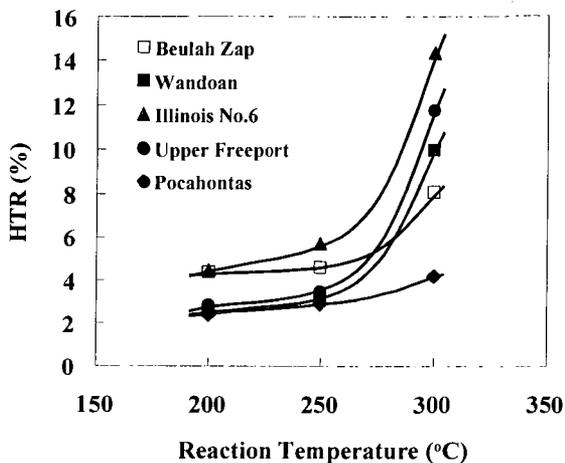


Figure 2. Effect of temperature on HTR of coal with  $[^3\text{H}]$ tetralin for 3 h.

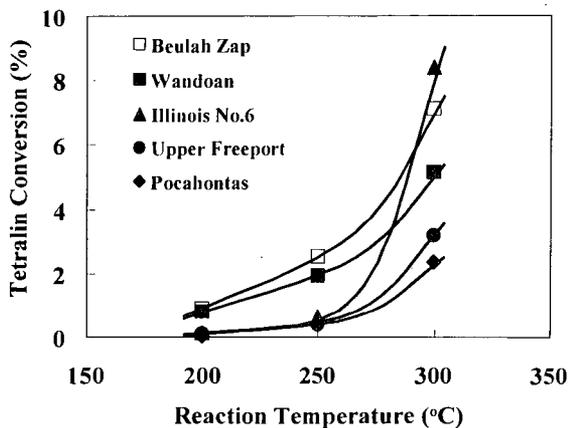


Figure 3. Effect of temperature on tetralin conversion in the reaction of coal with tetralin (3h).

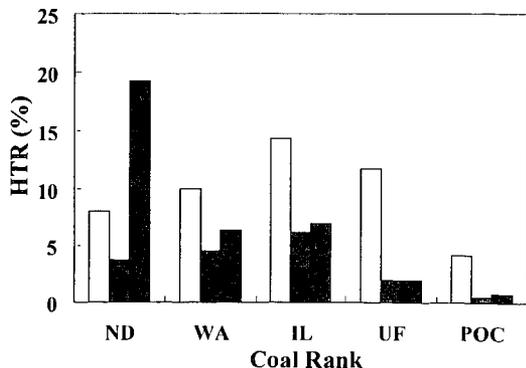


Figure 4. Comparison of HTRs of coals  
 □: Total HTR of coal with  $[^3\text{H}]$ Tetralin at 300 °C for 3 h  
 ◻: HTR of functional group in coal with  $[^3\text{H}]$ Tetralin at 300 °C for 3 h  
 ■: Total HTR of functional group in coal with  $[^3\text{H}]$ H<sub>2</sub>O at 100 °C for 6 h