COAL GEL CHEMISTRY 2. COAL LIQUIFACTION BY BINARY SOLVENT SYSTEM

Testuo Aida, Motohiko Satoh, Yasuhumi Shimoura, Masayuki Fujii

Department of Industrial Chemistry
Faculty of Engineering
Kinki University in Kyushu
11-6 Kayanomori, Iizuka, Fukuoka 820, JAPAN

INTRODUCTION

Although the importance of the accessibility of hydrogen donor solvents like a tetralin into coal matrix has long been emphasizing to the primary coal liquifaction of coal(1), not many efforts have been devoted to the study on the penetration mechanism of penetrants into coal, and developing practical devices of improving the accessibility.

Recently, we developed a new method for accurately measuring both the dynamic and equiliblium solvent swelling behaviors of coal(2), and revealed that the coal behaved as a molecular sieve which discriminated among molecules diffus ing into the pore system of coal on the basis of size, shape and functionality.

Based on our observations, tetralin is one of the penetrants which show significantly low degree of penetration rate into coal matrix, probably because of its steric hindrance. Meanwhile during the investigation of the synergistic effect on the solvent swelling of coal in the binary solvent system, of which one component was more less bulky than other, we also found that the steric requirement of coal could be released by forming "Coal Gel" under such condition.

Here we report the results of the study on the improvement of the accessibility of hydrogen donor like a tetralin into coal matrix, and the primay liquifaction of coal by using binary solvent systems.

EXPERIMENTAL

The swelling measurements were carried out as described into previous paper (2). Coal, Illinois #6, used in thses studies were from the Ames Laboratory Coal Library. Prior to use, the coal was ground, sized, dried at 110℃ overnight under vacuum and stored under nitrogen atmosphere. The solvents were distilled by ordinary procedures before use.

The coal liquifaction were carried out by using a stainless steel tubing micro-autoclave(8.0ml capacity). A typical coal liquifaction procedure is as follows: Coal(500mg; 50-60 mesh) and solvent(3.0ml) were taken into the autoclave with a stainless ball. After a nitrogen gas was bubbled through the mixture, it was heated for 2 hours in an electric oven maintaining temperature at 370 ℃, which was shaken for 3 minutes with 30 minutes intervals. After the reaction, the autoclave was cooled at room temperature, and carefully opened. The content was washed out with 50ml of distilled pyridine, and the mixture was immuersed in an ultrasonic cleaning bath for 2 hours. Then it was filtered through 3 μm Millipore-filter.

RESULT AND DISSCUSSION

1. Swelling of Illinois #6 Coal in Hydrocarbons

Table 1 shows the swelling data of Illinois #6 coal obtained with hydrocarbon solvents.

These data clearly indicate that there is a steric component to the swelling rate for solvent penetration of the coal matrix, for example, in the branched isomer, that is, in iso-propylbenzene the coal swelled aproximately 9 times slower than in n-isomer. On this point of view, it seems to be quite understandable that t-butylbenzene or tetralin are belonging to the slowest group of the penetrants. Actually, the molecular model of tetralin shows that the saturated ring system in this molecule makes a significant steric barrier upon the planer aromatic ring system.

2. Swelling of Illinois #6 Coal in Binary solvent System

Figure 2 shows the Illinois #6 coal in benzene / tetralin solvent system. There is a obvious synergistic effect on the equiliblium swelling ratio(Q-value) which means that the addition of certain amount of benzene to tetralin can make a significant increase of tetralin in the coal matrix in terms of the quantity and the penetration rate. As we reported previously(3), in this case also, the relative concentrations of each components, benzene and tetralin, in the supernatant of the coal-solvent mixture was varied through swelling, that is, the concentration of benzene was sharply decreased at the initial stage of swelling and then maintained almost constant value which was a little below the initial concentration.

These observations clearly indicate that less bulky benzene molecule penetrated predominantly into coal matrix, and formed so-called "Coal Gel" which will not possess such rigid steric requirement as the raw coal.

Table 2 shows the equilliblium swelling ratio(Q-value) obtained various solvent systems. It is obvious that the net volume of tetralin in the coal matrix in the binary solvent systems are significantly increased compared to tetralin alone.

3. Coal Liquifaction by Binary Solvent System

Figure 2 shows the pyridine solubles obtained from the liquifaction by the various binary solvent systems, in which the results by tetralin and THQ(1,2,3,-4-Tetrahydroquinoline) are also illustrated.

Here, some urguments may come to the penetration mechanism at the liquifaction temperature, 370℃, and the swelling measurement temperature, 21℃.

However the resultsd shown in this Figure strongly suggest that the enhancements of the yields of the liquifaction of coal were caused by the improvement of the accessibility of hydrogen donor like tetralin.

A curious phenomenon was also observed in the case of pyridine / tetralin system in which the addition of pyridine seemed to have induced a negative

effect on the coal liquifaction. It is quite interesting contrast to our common understandings that pyridine was one of the best solvents in the coal chemistry, i.e., extraction or swelling.

ACKNOWLEDGEMENTS

We wish to thank Professors Toshihisa Maeshima and Masakuni Yoshihara for their useful discussions and encouragements.

REFERENCES

1. M. B. Neuworth, D. Gray, "Fundamental Aspects of Primary Coal Liquifaction", Contractor Report, SAN85-7211, 1985
2. T. Aida T. G. Squires, Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem., 30, 95 (1985)
3. T. Aida, Y. Shimoura, M. Fujii, T. G. Squires, M. Yoshihara, T. Maeshima, Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem., Previous paper presented at this meeting(1988)

Table 1. Swelling Behaviors of Illinois #6 Coal in Hydrocarbons [a]

Hydrocarbons	Q-Value [b]	$V_{Ret.}$ [c]
n-Pentane	1.022	0.8
Benzene	1.046	1.0 [d]
Ethylbenzene	1.038	4.0
n-Propylbenzene	1.024	17.0
i-Propylbenzene	1.008	153
t-Butylbenzene	1.003	$> 10^3$
Tetralin	1.003	$> 10^3$

a) 100-200 mesh, measured at 21 ℃

b) After one month

c) Rate Retardation Factor : V_i (benzene) / V_i (hydrocarbone)

d) $V_i = 2.73 \times 10^{-4}$ min.$^{-1}$

Table 2. Swelling of Illinois #6 Coal in Binary Solvent System [a]

Solvent System	Q - Value [b]
Tetralin	1.003
n-Pentane	1.022
n-Pentane / Tetralin [c]	1.025
Benzene	1.046
Benzene / Tetralin [c]	1.030
Methanol	1.323
Methanol / Tetralin [c]	1.110
Pyridine	2.734
Pyridine / Tetralin [c]	1.482
NMPDN [d]	3.063
NMPDN [d] / Tetralin [c]	1.625

a) Coal: 100-200 mesh, measured at 21℃

b) After one month

c) Solvent / Tetralin (1 : 2 vol.)

d) N-Methylpyrrolidinone

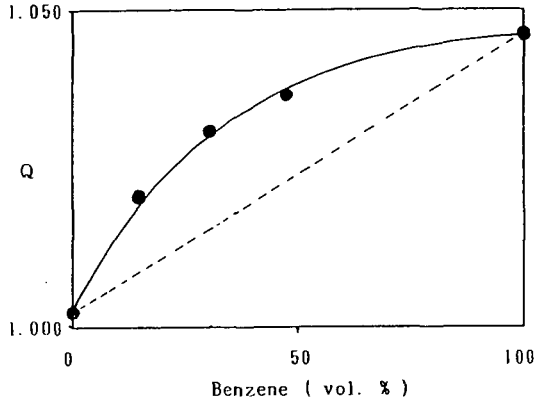
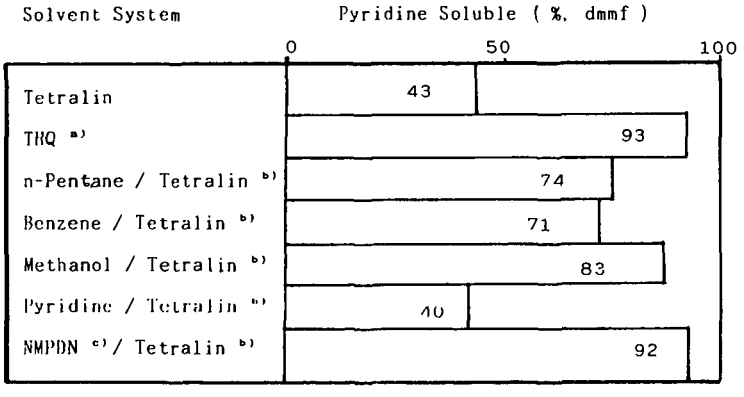


Figure 1 Swelling of Illinois #6 Coal in Benzene / Tetralin System (Coal: 100-200 mesh, 21 ℃)



a) 1,2,3,4,-Tetrahydroquinoline
b) Solvent / Tetralin (1:2 vol.)
c) N-Methylpyrrolidinone

Figure 2. Coal Liquifaction (Coal : 50-60 mesh, 370 ℃, 2 hrs.)