

CHANGE IN THE PORE SIZE DISTRIBUTION OF BROWN COAL ALONG WITH A PROGRESS OF MOISTURE RELEASE

Haruo Kumagai¹ and Kazuo Nakamura²

¹Center for Advanced Research of Energy Technology, Hokkaido University,
Kita-13, Nishi-8, Kita-ku, Sapporo 060-8628, Japan

²Research and Development Department, Osaka Gas Co., Ltd.,
6-19-9, Torishima, Konohana-ku, Osaka 554-0051, Japan

Keywords : pore, moisture release, macromolecular structure, CAMD

INTRODUCTION

Molecular modeling technique has been employed widely in biological chemistry to provide insight into the conformation, properties and interactions of biomolecules. According to existing development of molecular modeling software, the methodology has allowed treatment of relatively large molecules and has begun to be applied to fuel chemistry by constructing complex heterogeneous macromolecular model. Carlson [1] applied computer-aided molecular design (CAMD) methods to determine three-dimensional minimum-energy conformations for four bituminous coal models. He indicated that nonbonding interactions, in particular, van der Waals and hydrogen bonding interactions, are strong driving forces to form and stabilize the structures of the coal models. Takanohashi and co-workers also determined the minimum-energy conformation of a bituminous coal by a CAMD method and suggested that the coal has a possibility to have an associated structure of constituent molecules in the coal having a continuous distribution of molecular weights [2,3].

Low rank coals such as lignite and brown coal are featured by their high residual moisture contents in the range from 30 to 70wt%. Because of such a high moisture content, moisture removal is the primary and essential step in almost all brown coal utilization processes. Furthermore, the drying step is known to have a significant effect on the physical and chemical characteristics of the dried coal. For example, it has been suggested that drying have negative impact on liquefaction reactivity [4-7] and that in lignite liquefaction the oil yield is higher for dried coal than that for raw or partly dried one [8]. These nominal impacts of drying on the conversion reactivity can be attributed to an irreversible change of pore structure that results in a limitation of accessibility of reacting components [9]. And it is easy to imagine that the pore structure change is brought about by the change in macromolecular structure of coal along with drying.

In a previous paper [10], we investigated the change in conformation for an Australian brown coal with its moisture removal process by means of a CAMD method. The results indicated that change in conformation of the coal simulated by CAMD method is well corresponding to the observed volumetric change, and removal of water molecules results in a drastic conformational change in the final stage of moisture removal. In the present study, conformations of an Australian brown coal are simulated under 3D periodic boundary conditions in order to elucidate the change in the pore distribution along with a progress of moisture release.

CAMD calculation method

The CAMD study was carried out by using an O₂ workstation (Silicon Graphics, Inc.) with Cerius² software (version 3.8, Molecular Simulations Inc.). The software is capable of calculating the most stable structures with the minimum conformational energies using COMPASS, UNIVERSAL and DREIDING force fields. Since our previous study indicated the importance of hydrogen bonding interactions on the stabilization of brown coal conformation,

the DREIDING 2.21 force field was used in this study. Cerius² software allows the use of periodic boundary condition, in which model molecules are placed in a unit cell surrounded by the same cells in all directions. Molecular segments in the cell can interact with others in the neighboring cells as well as in the same cell. If a segment exits on the one surface of the cell, the same one enters from opposite side. The structure of Australian brown coal (Yallourn brown coal ; YL) was modeled by two oligomers, namely a pentamer (Mw=1892) and an octamer (Mw=3074), of unit structure. The unit structure, which was constructed on the basis of the data from elemental analysis and ¹³C-NMR spectroscopy of the coal [11], is shown in figure 1. Each oligomer was specially arranged so as to have no interaction with others. Simulations of moisture removal process were initiated by generating 413 water molecules (59.95wt%, wet basis) surrounding the model molecule and the **minimum energy conformation (MEC)** for the model with water molecules was calculated based on molecular mechanics and molecular dynamics methods. After MEC was obtained, the volume and density of unit cell and pore distribution were calculated. The pore volume was defined as prove occupiable volume using several size of spherical probe in radius from 0.5Å to 3.0Å. The calculation was repeated decreasing the number of water molecules step by step to 0, and finally MEC for model molecule with 0 water, i.e., completely dried coal was obtained.

RESULTS AND DISCUSSIONS

Change in the volume and in the density of MEC unit cell which contain model molecules of YL and water molecules are shown in figure 2 as a function of the extent of moisture removal (%). During moisture release process, the volume decreases monotonously with moisture removal, and reaches nearly a half of initial volume. Initial density of the cell (1.110 g/cm³) is in a good agreement with experimentally determined raw coal density [12, 13], while density of the cell for completely dried YL (0.929 g/cm³) is slightly higher than mercury density of dried YL (0.873 g/cm³). As shown in figure 2, density of the cell decreases gradually with the extent of moisture removal up to 80%. A significant decrease in density of the cell is observed with the extents higher than 80%. In the previous study [10], we demonstrated that change in the volume for YL model molecules without water molecules proceeds in the final stage of moisture removal at which non-freezable water is removed, and the change in volume corresponds well to the change of non-bonding interaction energies. The significant decrease in density observed in this study is well in harmony with the previous study. Thus, the result indicates that the dense conformation of YL model molecules with water molecules changed to porous one with removal of non-freezable water.

Micropore size distribution is calculated from occupiable volume with spherical probe, V_{occ} , and radius of the probe, R_p . The micropore size distribution curves, dV_{occ}/dR_p vs R_p , are shown in figure 3. The micropore size distribution is little affected with extent of moisture removal at the range from 0% to 65%. As we can expected from change in the cell density, described above, a significant change in the distribution is observed with the extents higher than 80%. The change in micropore size distribution shows the enlargement in pore size that has occurred at the final stage of moisture removal. The total micropore volume increases from 0.15 cm³/g for wet YL (0% moisture removal) to 0.30 cm³/g for completely dried coal, down to a micropore size of 0.5Å. The change corresponded well to the change of density.

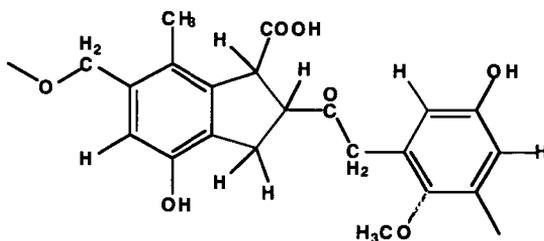
Although techniques are available for the characterization of the micropore structure of dried coal, there are no equivalent procedures to determine the micropore structure of coal in a wet state. Setek and co-workers [14] have applied small angle X-ray scattering (SAXS), and CO₂ sorption technique to determine the microporosity of YL. The micropore volumes for dried YL show reasonable agreement by the two techniques (0.058 cm³/g for CO₂ sorption, 0.060 cm³/g for SAXS) and slightly larger than comparable micropore volume ($R_p > 2.75\text{\AA}$) obtained by CAMD (0.032 cm³/g). The micropore volume for wet YL obtained by SAXS (0.110 cm³/g) is much

larger than that calculated by CAMD ($0.001 \text{ cm}^3/\text{g}$). This probably reflects differences in the size of the structures to determine the microporosity of brown coal.

In summary, the change in volume and density for YL model molecule with its moisture release process could be successfully simulated by using the CAMD method. Although the coal model molecule employed in this study is rather simple and small, the results appear to represent the characteristics of the brown coal, at least change in the density and micropore size distribution along with a progress of moisture release.

REFERENCE

1. Carlson, G.A. *Energy Fuels* 1992, 6, 771.
2. Takanoashi, T.; Iino, M.; Nakamura, K. *Energy Fuels* 1994, 8, 395.
3. Nakamura, K.; Takanoashi, T.; Iino, M.; Kumagai, H.; Sato, M.; Yokoyama, S.; Sanada, Y. *Energy Fuels* 1995, 9, 1003.
4. Gorbaty, M.L. *Fuel* 1978, 57, 796.
5. Atherton, L.E. *Proc. Int. Conf. Coal Sci.* 1985, 553.
6. Neavel, R. *Fuel* 1976, 55, 237.
7. Cronauer, D.C.; Ruberto, R.G.; Silver, R.S.; Jenkins, R.G.; Davis, A.; Hoover, D.S. *Fuel* 1984, 63, 77.
8. Vorres, K.S.; Wertz, D.L.; Malhotra, V.; Dang, Y.; Joseph, J.T.; Fisher, R. *Fuel* 1992, 71, 1047.
9. Vorres, K.S.; Kolman, R.; Griswold, T. *Prepr. Pap. Am. Chem. Soc., Div. Fuel Chem.* 1988, 33 (2), 333.
10. Kumagai, H.; Chiba, T.; Nakamura, K. *Prepr. Pap. Am. Chem. Soc., Div. Fuel Chem.* 1999.
11. Yoshida, T.; Narita, Y.; Yoshida, R.; Ueda, S.; Kanda, N.; Maekawa, Y. *Fuel* 1982, 61, 824.
12. Higgins, R.S.; Kiss, L.T.; Alladice, D.J.; George, A.M.; King, T.N.W. *SECV Research and Development Department Report No. SC/80/17*
13. Higgins, R.S.; Kiss, L.T.; George, A.M.; King, T.N.W.; Stacy, W.O. *SECV Research and Development Department Report No. SC/81/28*
14. Setek, M.; Wagerfeld, H.K.; Stacy, W.O.; Kiss, L.T. *Fuel* 1983, 62, 480



C:65.6, H:5.2, O:29.2 wt%

Mw:384.37

H-bond acceptor:7, H-bond donor:3

Figure 1. Unit structure assumed for YL model molecule.

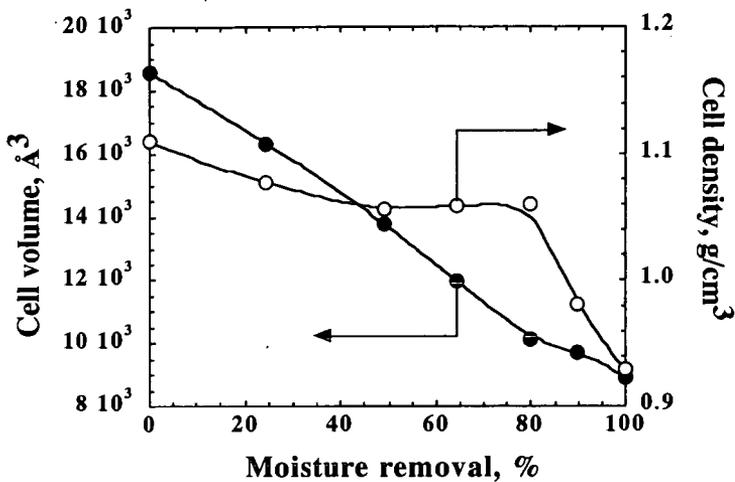


Figure 2. Change in the cell volume and density with extent of moisture removal.

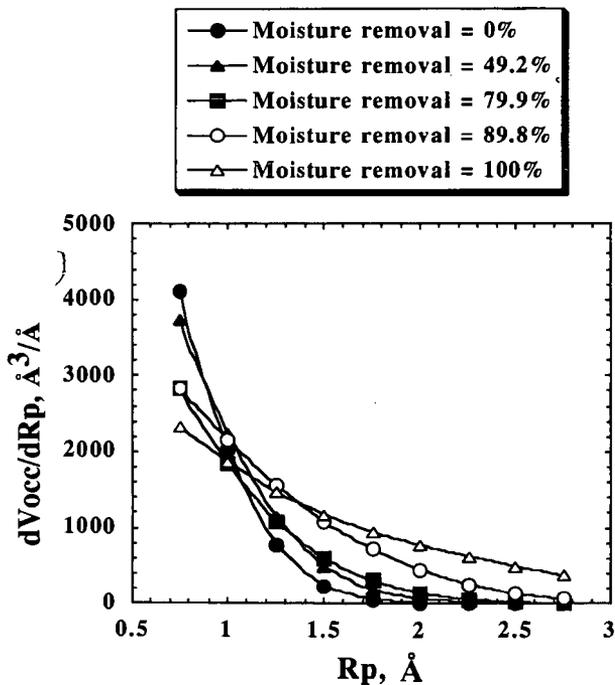


Figure 3. Micropore size distribution curves.