CHEMISTRY LETTERS, pp. 1563-1566, 1990.

Chemical Constituents of Macromolecular Phase of Akabira Coal

Masakatsu NOMURA,* Kenji MATSUBAYASHI, and Mikio MIYAKE
Department of Applied Chemistry, Faculty of Engineering,
Osaka University 2-1, Yamadaoka Suita, Osaka 565

A Residue fraction from extraction of Akabira coal was analyzed by Curie point pyrolysis, which showed a great increase of volatile from at 500 °C to 590 °C. A GC-MS analysis of the volatile at 590 °C indicated an evident appearance of phenol derivatives, in a series of alkane, alkene, cyclohexane, benzene, and naphthalene derivatives. SEM observation indicated that pyro-coke at 590 °C melted while that at 500 °C remained unchanged. Therefore, the abruptly increasing volatile at 590 °C originates mainly from macromolecular phase of coal.

Since Wheller1) had proposed the concept that coal organic materials consist of two components, many coal chemists have been engaged in this concept, active discussion about this being done among them. Larsen2) and Jurkiewicz3) have reported that two components, such as three dimensionally bridged and solvent-insoluble polymeric portion and linearly linked and solvent-soluble materials form an organic portion of coal while Given,4) Marzec,5) and Jackson6) are insisting that coal is composed of macromolecular network structure in which low-molecular-weight materials are trapped through their physical interaction with macromolecular networks. However, there seems to be little information about what sort of chemical components contribute to this macromolecular network structure. Macromolecular network structure is considered to exist mainly in a solvent-insoluble polymeric portion so that a residual portion from solvent extraction of coal seems to be an appropriate target for above mentioned analysis. Therefore we have employed a Curie point pyrolysis technique to get more detailed information about chemical components of macromolecular structure where SEM observation of a pyro-coke from this pyrolysis is examined because a lot of coke is retained on the pyrofoil after pyrolysis, the information about the coke being essential. Akabira coal pulverized under 100 mesh was submitted to solvent extraction using CS_2-N-methyl-2-pyrrolidone,[7] the method of which was modified as follows: Akabira coal, 8 g was extracted with the binary solvent under ultrasonic irradiation for 30 min. This extraction was carried out 7 times until color of the filtrate disappeared. In 32.8 wt% and 67.2 wt% the extract and the residue were obtained, respectively. The extract was separated into WS [soluble in acetone-water (2:8)], AS [insoluble in acetone-water (2:8)], PS (pyridine soluble), and MS (pyridine insoluble).[8]

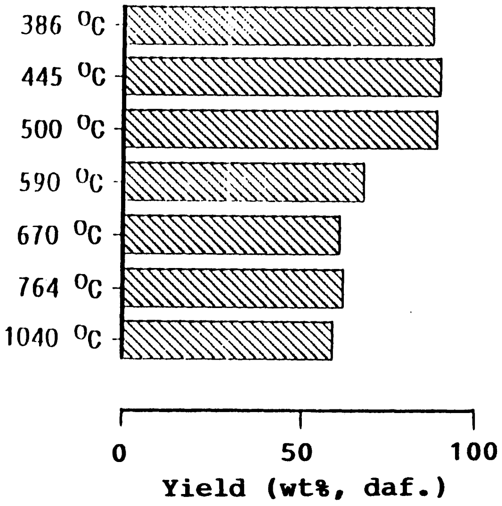

Fig. 1. Yield of coke in pyrolysis of residue fraction, 386 °C - 1040 °C, 3 s.

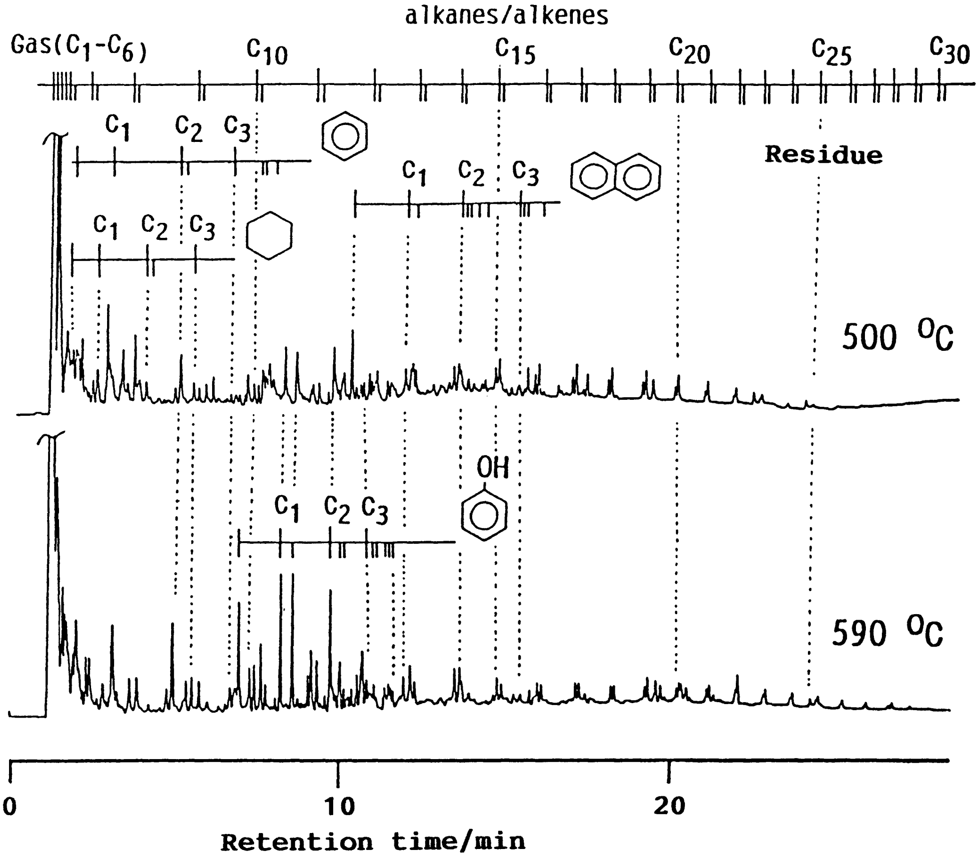

Fig. 2. Pyrograms and assignment of compounds of residue fraction at 500 °C and 590 °C, 3 s.

Jurkiewicz[3] had stated that coal organic materials should be separated into mobile and immobile fractions, the former and the latter corresponding to molecular phase and macromolecular phase, respectively. Mobile fraction was considered as a solvent-soluble

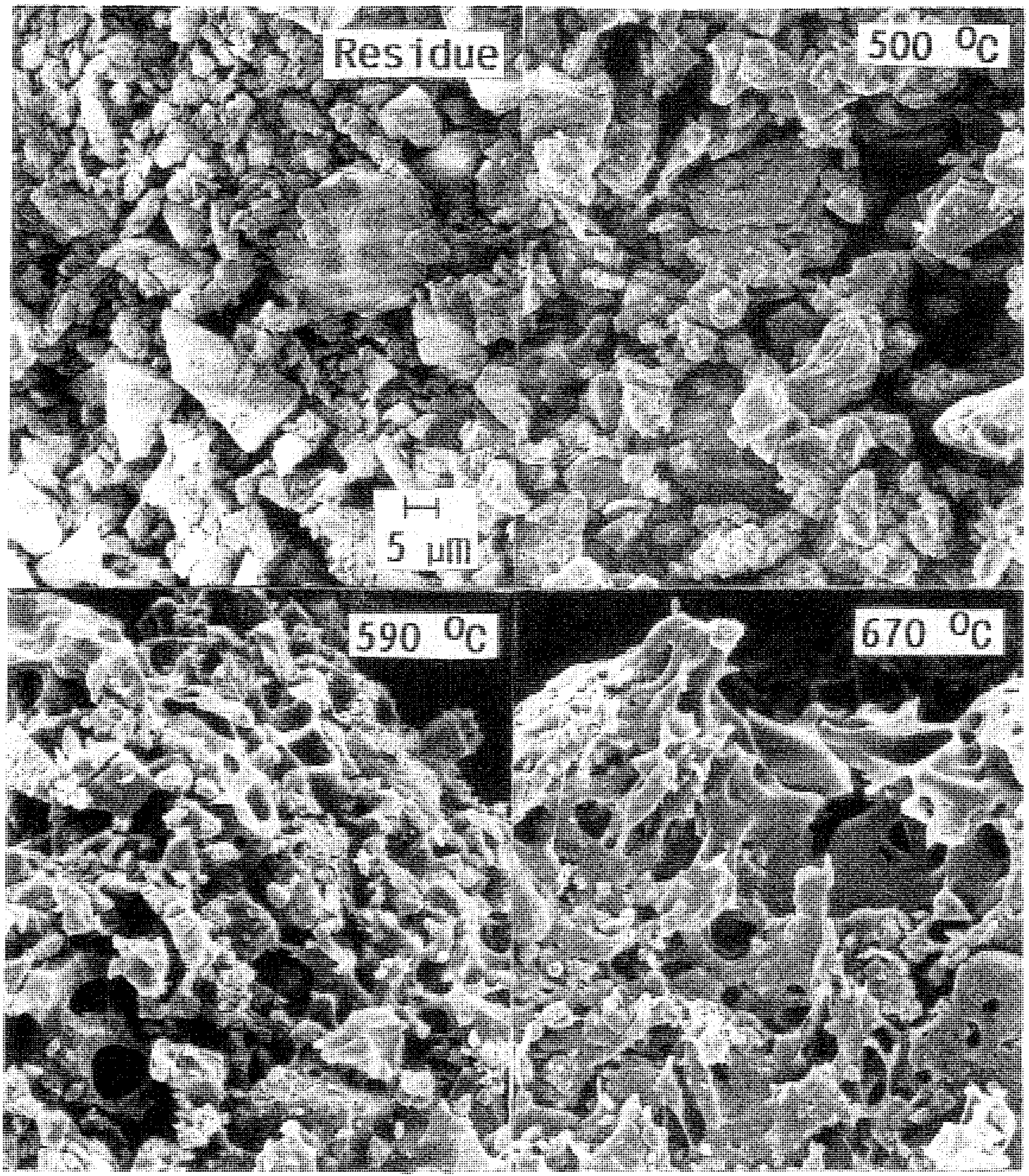

Fig. 3. Scanning electron photomicrographs of coke from pyrolysis of the residue fractions at 500 °C - 670 °C, 3 s, together with the residue fraction itself (x 1000).

fraction. We have examined a Curie point pyrolysis of AS, PS, and residue (major fractions) at 670 °C for 3 s and a volatile amount [100x(weight of sample - weight of coke remained on a pyrofoil)/weight of sample] from these three fractions reached to 46 wt% based on total organic portion of coal.

In order to examine which phase, macromolecular phase or molecular one, contributes mainly to chemical constituents on pyrogram at 670 °C for

3 s, Curie point pyrolysis was carried out at 7 different temperatures using residue fraction. Figure 1 shows results of the pyrolysis. From Fig. 1, a sharp difference of a volatile amount was observed between at 500 $^{\circ}$C and at 590 $^{\circ}$C: Up to 500 $^{\circ}$C, about 10 wt% of a volatile portion was obtained, however, above 590 $^{\circ}$C this volatile amount increased up to 30 wt% based on the weight of residue fraction. Figure 2 indicates the assignments of compounds in a volatile portion on GC, which was undertaken using high resolution mass spectro-meter (JEOL DX 303). At 590 $^{\circ}$C, very sharp peaks, the compounds of which could be assigned as alkylphenol derivatives appeared on the pyrogram along with a series of alkane and alkene, alkylcyclohexane, alkylbenzene and alkylnaphthalene derivatives. A sharp increase of volatile amount observed at 590 $^{\circ}$C could be correlated to a relaxation of network structure of coal. If the case is so, surface of pyro-coke at 590 $^{\circ}$C seems to be somewhat different from the surface of pyro-coke at 500 $^{\circ}$C, so the SEM photographs were taken using a Hitachi S-800 type instrument. Figure 3 indicates the surface of pyro-coke at different temperatures. At 500 $^{\circ}$C, surface of pyro-coke shows no change compared with that of original residue fraction. However pyro-coke at 590 $^{\circ}$C distinctly indicates that the residue fraction surely melted during this rapid heating, this strongly suggesting that new components of volatile portion comes from the breaking of bonds of macromolecular phase so called network structure of coal organic materials. According to measurements of FT-IR spectra of AS, PS, and residue by JEOL JIR-AQS 20M type spectrometer, OH groups (based on relative concentration at 3343 cm^{-1}) contained in the residue are more than those of solvent-soluble fractions such as AS and PS. This finding seems to support strongly our present proposal that, at more than 590 $^{\circ}$C, phenol derivatives, that is, increasing chemical constituents appeared on the pyrogram of residue come mainly from macromolecular phase.

References

1) R. V. Wheller, J. Chem. Soc., 103, 1715 (1913).
2) T. K. Green and J. W. Larsen, Fuel, 63, 1538 (1984).
3) A. Jurkiewicz, A. Marzec, and N. Pisewski, Fuel, 61, 647 (1982).
4) J. S. Youtcheff, P. H. Given, Z. Baget, and M. S. Sundaram, Org. Geochem., 5, 157 (1983).
5) H. R. Schulten and A. Marzec, Fuel, 65, 855 (1986).
6) P. J. Redlich, W. R. Jackson, and F. P. Larkins, Fuel, 68, 231 (1989).
7) M. Iino, T. Takanohashi, H. Osuga, and K. Toda, Fuel, 67, 1639 (1988).
8) K. Matsubayashi, M. Nomura, and M. Miyake, Chem. Lett., 1990, 291.

(Received June 8, 1990)