R. Copy of Argonne Scientists' article of rapid production of coal

TECHNOLOGY

Argonne Scientists Make Artificial Coal

Process using clay catalysts to transform lignin provides new insights into coal structure and how to alter it

Study of the basic chemical structure of coal has led to new ideas about the way coal was formed during geologic time. Chemists at Argonne National Laboratory have succeeded in making a type of artificial coal from naturally occurring materials. The process is much less severe than formerly thought to be necessary and provides some new insights into coal structure and how to alter it.

The most widely held view of natural coalification—the sum of the geological processes that produced coal—is that organic plant material was transformed microbially to humic materials. These, in turn, were transformed by abiotic thermal processes to lignite, bituminous coal, and anthracite.

Randall E. Winans, who leads the group from Argonne's chemical division investigating coal structure, says that as appealing as this view may be, it is no more firmly based than other views. In fact, he maintains, there is no incontrovertible evidence to support any particular theory of coalification. How coal was formed is still under debate.

In this context it appears significant that Winans' group recently has demonstrated that artificial coalification reactions catalyzed by clay minerals easily transform lignin into an altered lignin that is much like that found in natural lignite. So it appears that the group has made some artificial lignite.

Winans believes that the early results in the project support the idea that, in the natural coalification processes, much of the lignin survives the early diagenetic stage with little or no alteration of its chemical structure. Subsequently, it is transformed into aromatic-rich coal macromolecules (vitrinite) during the catalytic phase of coalification.

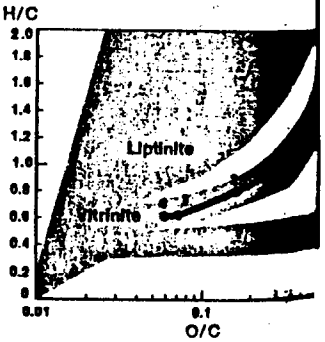
Most of the plant materials that were converted to coal were probably woody varieties, and the chief interest is with these materials. Coalification of woody tissue appears to be primarily a loss of oxygenated compounds, mostly carbohydrates, followed by the direct chemical alteration of lignin to the macromolecules found in coal. The present study is examining the possibility that most, if not all, of the vitrinite macerals in lignite were formed directly from slightly altered lignin.

The general approach that Winans' group is using includes three stages. The first is to determine the chemical identity of lignin, kerogens found in shale, and various coals by use of selective oxidative degradation, pyrolysis and other suitable means. This is followed by the transformation of lignin into artificial coal products by low-temperature catalytic reactions. Clays form the family of catalysts. The final stage is comparison of the natural and artificial coal macerals. The presumption is that close correspondence will help deduce the processes of coalification and, more important from a scientific viewpoint, the detailed structure of coal.

Clay minerals have been long known to exert catalytic effects on lignin. In the Argonne experiments a typical example would involve heating of clay and lignin mixtures to temperatures from 150 to 200 °C. The yield of insoluble products ranges from 54 to 67% by weight with longer reaction times favoring more vitrinitic materials. There is an increase in aromaticity with time that generally parallels that observed for natural coals of increasing rank. Likewise, the general indications are that the processes at work in the artificial coalification are similar to those occurring in natural evolution. A typical experiment would run for more than two months.

The oxidation results are also supported by a ^{13}C nuclear magnetic resonance study of softwood lignin using cross polarization and magic angle spinning. Demethoxylation occurs very rapidly and

H/C, O/C ratios provide coalification road map



The progress of coalification be measured in terms of the hydrogen-to-carbon and oxygen-to-carbon ratios. There are three general paths. Argonne's artificial coalification experiments, generally, follow the line shown, from upper right to lower left. For example, lignin was subjected to artificial coalification for two months to yield the modified form at point 1. Longer times yielded the subsequent points 2, 3, and 4

Appendage R.