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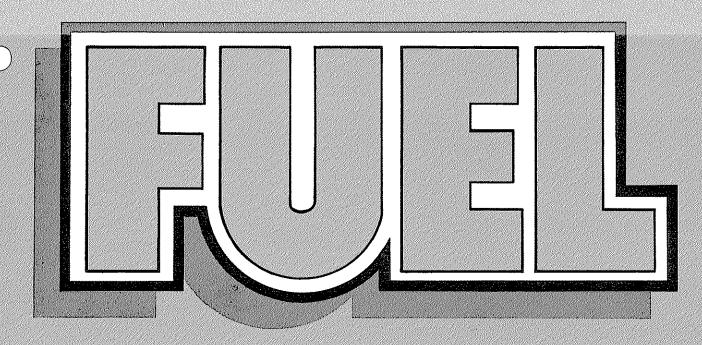
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Structure of coals and their conversion to gaseous fuels*

Philip L. Walker, Jr.
Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, USA

It is now generally agreed that all coals (except anthracites) have as their main building blocks aromatic and hydroaromatic structures, some containing heteroatoms and other functionalities, consisting of three to five rings crosslinked primarily by ether oxygen and methylene bridges. The presence of both crosslinks and hydroaromatic linkages in the building blocks between aromatic groups, prevents good alignment of the building blocks. This results in extensive microporosity in coals and affects the apparent molecular weight of the material.

Prior to, or concurrent with, conversion of coals to gaseous fuels, pyrolysis takes place as the coal is heated to reaction temperatures. Two fundamental factors are of importance and, hence, should be considered during pyrolysis: (1) changes in the nature of the porosity in the solid; and (2) the presence of nascent, active carbon sites.

Upon heating, coals behave more or less like thermoplastic organic precursors, depending on the nature of the building blocks of the coals. The extent to which they become fluid primarily depends upon the number and thermal stability of the crosslinks which are present in the solid at temperatures between ≈ 400–$450°C$. If crosslinking at these temperatures is low, as with most bituminous coals, significant fluidity develops, building block alignment occurs and much of the open microporosity which existed in the original coal is lost. The bituminous coal behaves like a thermoplastic precursor, swelling and bursting as volatile matter is lost during heating. Preoxidation of bituminous coals at 200–250°C is seen to reduce significantly the fluidity and prevent the decrease in the surface area on subsequent heating to 400–450°C. This results in a marked enhancement of the reactivity of the resultant carbonaceous solids (chars).

The thermosetting precursors (lignites), conflicting processes occur upon pyrolysis. Liberation of volatiles results in the generation of additional porosity in the solid, thus enhancing its reactivity. Thermal breakage of crosslinks and conversion of hydroaromatic groups to aromatic groups and then to small carbon crystallites allows the building blocks to align preferentially, this resulting in decreasing porosity in the solid, thus reducing its reactivity.

During the liberation of volatiles upon coal pyrolysis, free radical carbon sites at the edges of the building blocks are generated, these are designated as nascent active carbon sites. These nascent sites have a fleeting lifetime; but if a collision event between a gaseous species and such a site occurs before it rehybridizes to a less active site, the probabilities of both carbon gasification and carbon deposition reactions occurring are much enhanced. Thus, the introduction of hydrogen into the reactor during pyrolysis leads to a substantial increase in the yield of volatiles owing to both enhancement of the carbon gasification rate via methane production and reduction in carbon deposition rate from tars.

The reactivity to gasification of chars produced by rapid pyrolysis of lignites is greater than that of chars produced by slow pyrolysis. Reactivity decreases as the holding time increases at pyrolysis temperatures, owing to surface annealing which reduces the number of nascent carbon sites and, hence, the active surface area of the char.

Chars produced from American lignites have reactivities to O_2, H_2O and CO_2 which are up to 150 times higher than reactivities of cokes produced from bituminous coals. However, smaller differences are found for the reactivities of chars and coals in hydrogen than in oxygen-containing gases.

Lignites, loaded with calcium by acidification and cation exchange[1], show an increase in reactivity to gasification by water at 650°C as the calcium content increases. However, these lignites show a decrease in reactivity to gasification in hydrogen. This is attributed, primarily, to calcium being an excellent catalyst for carbon gasification in oxygen-containing gases, but a poorer gasification catalyst in hydrogen. Calcium in American lignites is very much better dispersed than in bituminous coals, where it occurs as calcite; hence the greater reactivity of lignite to oxygen-containing gases.

Other inorganic cations catalyse gasification reactions to a greater or lesser extent than calcium. For gasification by H_2O and CO_2, potassium and sodium are very good catalysts, but magnesium is a poor catalyst. Gasification in H_2 and CO is catalysed by iron, but potassium and sodium, like calcium are poor catalysts.

The ease of converting coal chars to gaseous fuels is seen to depend upon: (1) concentration of active carbon sites; (2) accessibility of reactive gases to the active sites through the pore system of the char via feeder pores (macropores); and (3) concentration and dispersion of inorganic species present which act as specific carbon gasification catalysts.

In order to study successfully these catalysed carbon gasification reactions, several fundamental research problems have to be overcome:

(1) How to measure catalyst dispersion.

(2) Decomposition of metal salts over the carbon active sites; e.g. K_2CO_3 decomposes faster over carbon surfaces than in bulk.

(3) The activity of active sites in the absence and presence of carbon gasification, as measured by exchange reactions.

(4) Optimum ways of catalyst addition to coals to get maximum (optimum) dispersion.

(5) Interactions of cations and impregnants with mineral matter already present in the coals.

(6) Low-temperature oxidation of caking coals.

The use of radioactive isotopes would allow many of these problems to be resolved.

REFERENCES

1   Hippo, E. J., Jenkins, R. G. and Walker, P. L. Jr. *Fuel* 1979, **58**, 338