Early Stages of Coal-Carbonization:
Evidences for Isomerization Reactions*

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At temperatures between ∿350° and 425°C, the molecular structures that charac-
terize coal are rapidly, and very obviously, transformed into more stable carbon con-
figurations through loss of "volatile matter" (as tar and gas). But little is known
about possible configurational changes at lower temperatures. Thermograms of coal (1)
indicate specific heat effects as endo- and exotherms from ∿200°C up; but because en-
thalpy changes recorded in this manner include sensible heats as well as heats of
reaction, it is difficult to assess the nature of the chemical processes which produce
the thermograms. On the other hand, low-temperature chemical changes, if such did in
fact occur, should be reflected in the "reactivity" of heat-treated coal - and, in
particular in its response to oxidation; and if oxidation could be performed so as to
yield identifiable products, it should be possible to detect the major configurational
changes in the distribution of oxidation products.

Accordingly, since it was previously shown (2) that sodium hypochlorite oxida-
tion yields relatively simple carboxylic acids of which many could be identified by
gas chromatography (GC) and mass spectrometry (MS), we thought it pertinent to deter-
mine whether this technique, although involving still not fully understood reaction
paths, could also be used to monitor low-temperature changes in coal. The present
paper reports the first results of such an exploratory study.

Experimental and Results

For the purposes of this investigation, two coals - a Western Alberta lvb coal
with C = 90%, and a Kentucky hvb coal with C = 85% - were used.

10 g samples of these coals, each sized to -60 +115 mesh, were preheated in
helium for 2 hr at the desired temperature, cooled, and then stored under pure He
until required. No significant weight losses or changes in elemental compositions
were observed with either coal up to 375°C, but 5-10% weight losses, and slight (0.5-
1.2%) increases in carbon contents, with corresponding reductions in oxygen were noted
after preheating at 390-400°C.

For the oxidation experiments, 2 g (preheated) samples were first "activated"
by reaction with nitronium-tetrafluoroborate in acetonitrile, and thereafter treated
with 125 ml of an aq. 1.6 N sodium hypochlorite solution at 60°C. The pH of the re-
action mixture was maintained at 12 by adding NaOH pellets at regular intervals. When
reaction was complete, the mixture was acidified; insoluble matter was filtered off;
and soluble carboxylic acids were extracted with ether. The residual solution was
freed of water by low-pressure distillation at 40°C, and solid material left behind
was extracted with anhydrous methanol.

The ether- and methanol-extracts were then combined, converted to methyl esters
by reaction with diazomethane, and separated by gel permeation chromatography on a
(Water Associates') Poragel column into two fractions with molecular weights >600
and <600 respectively (fractions A and B). Fraction B (mol. wt. <600) was further
subdivided into "simple" (B,1) and "complex" (B,2) acids by elution chromatography
on a Florisil column. (From this column, methyl esters of "complex" acids could only

be eluted with 10:1 chloroform-methanol, while esters of "simple" acids could be taken off with pentane, hexane and 2:1 hexane-chloroform.)

The "simple" acids (fraction B,1) were quantitatively analyzed by GC on OV-17/ Chromosorb WHP and reference to peak area vs. concentration diagrams for authentic compounds. Where no authentic compounds were available for methyl esters of toluene carboxylic acids, concentrations were computed from response factors derived from those appropriate for the methyl esters of benzene carboxylic acids.

Detailed study of the oxidation products showed that the raw and variously preheated coals furnished substantially identical amounts of carbon dioxide (Figure 1), but that there were significant, though complex, variations in the yields of carboxylic acids (Figures 2-6) and that these yields depended on the nature of the coal as well as on the preheat temperature. Thus, while the lvb coal had to be preheated to at least 350°C before it produced greater than the initial amounts of carboxylic acids, the hvb coal needed only to be preheated to 200°C before doing so (Figure 2).

These observations accord well with enthalpy changes recorded by differential thermal analysis (1), and are, in our view, clearly indicative of thermally induced alterations of the initial carbon configurations in the two coals.

Fraction A - composed of acids with mol. wts. in excess of 600 - presumably represents condensed aromatic fragments of the original and heat-treated samples; and if so, the fact that yields of this fraction increase with preheat temperatures suggests that aromatization begins at temperatures as low as 150°C in hvb coal and at ∿200°C in lvb coal (Figure 3).

Fraction B,2 - which represents over 50% of the total acid product from each sample and consists of "complex" acids with mol. wts. <600 - can be tentatively identi-fied as originating in coal fragments that produce "pre-asphaltenes" in coal liquefac-tion processes (3), and variations of the yield of this fraction with preheat tempera-ture are also interesting (Figure 4). In the case of lvb coal, B,2 yields reach a maximum at 375° and then decline precipitously at 390°C, but the decline is compen-sated by an almost eqivalent increase in the yield of high molecular weight (>600) material. In contrast, B,2 yields from the hvb coal attain a maximum at 200°C, fall to minimum at 300°C, and then rise to another maximum at 400°C.

The "simple" acids with mol. wts. <600 (fraction B,1), which were completely characterized and invariably accounted for 22-30% of the total acid products, are evidently produced from easily oxidizable open structured coal fragments; and from the lvb coal, the yield of this fraction decreased steadily as preheat temperatures rose. However, in the case of the hvb coal, the yield was found to remain constant up to 300°C, and to fluctuate thereafter (Figure 5).

Finally, some note must be taken of the distribution pattern of penta- and hexa-carboxy benzenes vis-a-vis that of tri- and tetra-carboxy toluenes. Quite gen-erally, maxima for benzenes and almost coincident with minima and maxima of toluenes. But here again, significant differences between lvb and hvb coal are observed. For the lvb coal, maxima of benzenes lie at 175° and 375°C, while for the hvb coal, they appear at 350° and 400°C. Maximum yields of toluenes were obtained from lvb coal after preheating at 300°C, and from hvb coal after preheating at 150°C (Figures 6 and 7).

We believe that these variations in yield and distribution of carboxy acids are best understood in terms of low-temperature intra-molecular isomerization re-actions which modify the initial carbon-hydrogen configurations of the coal well before it begins to undergo thermal cracking. Of the two specific processes that could be postulated as effecting such isomerization, one is trans-annular bond

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formation (Figure 8) and the other is isomerization of benzylic carbon to methyl-phenyl derivatives (Figure 8) and more complex ring systems. Either change could readily occur at temperatures as low as 150°C and create structures susceptible to oxidation by sodium hypochlorite.

We note, in this connection, that ether-oxygen also appears to play a major role in the behaviour of coal at elevated temperatures (4); but whether or not iso-merization and/or cleavage of ether-linkages also occur at low temperatures could not be determined in this study, since hypochlorite oxidation easily degrades hetero-cyclic functional elements under acidic as well as basic conditions.

References

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3. D. D. Whitehurst and T. O. Mitchell; ACS Div. Fuel Chem. Preprints 21 (5), 127 (1976)

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4. L. Lazarov and G. Angelova; Fuel (Lond.) 50, 338 (1971

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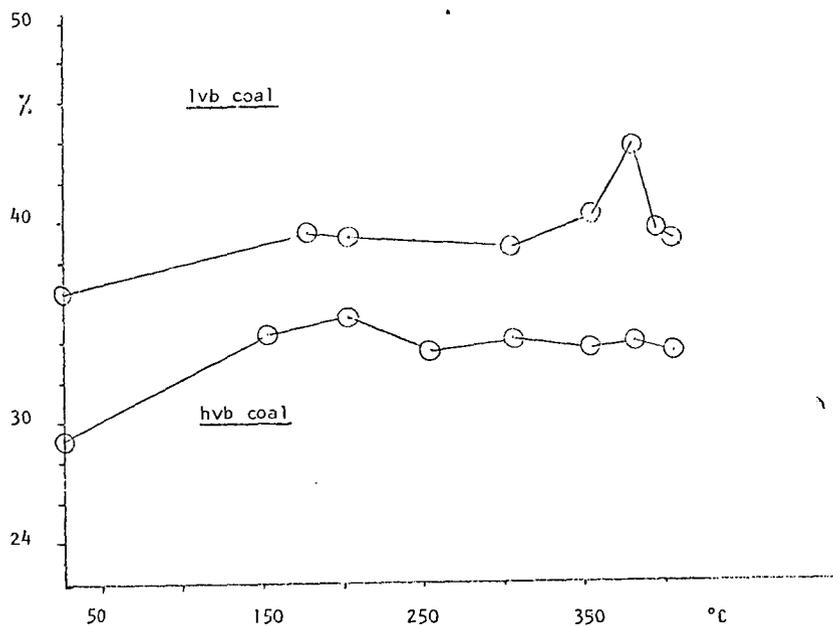
    B. Ignasiak and M. Gawlak; Fuel (Lond.) 56, 216 (1977)

Fig. 1 Yield of CO_2 as per cent of coal-carbon from variously heat-treated samples
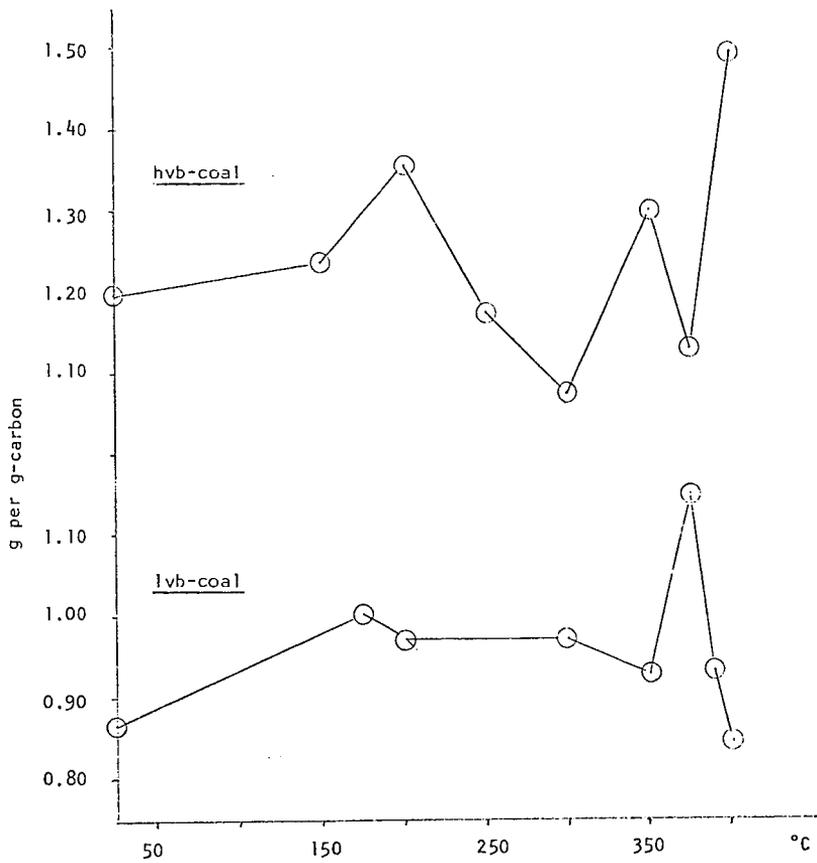
Fig. 2   Yield of total carboxylic acids as methyl
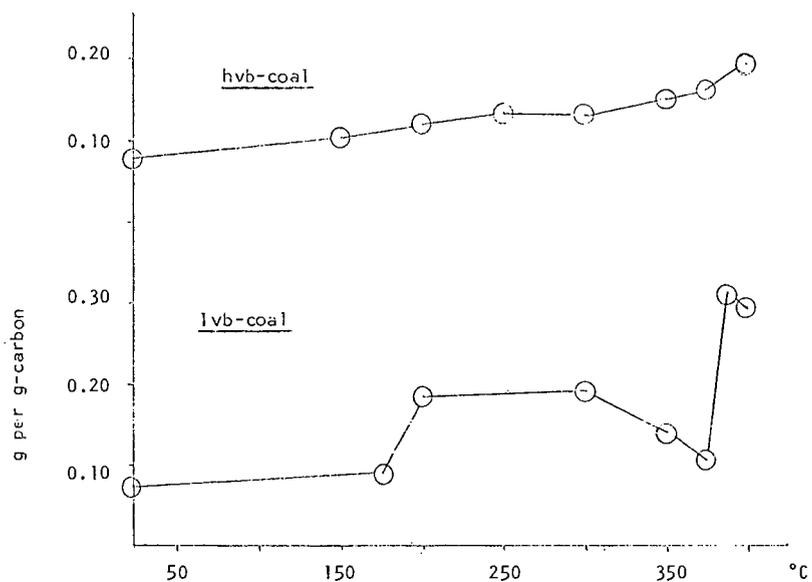   esters from variously heat-treated samples.

Fig. 3 Yield of 'complex acids' as methyl esters
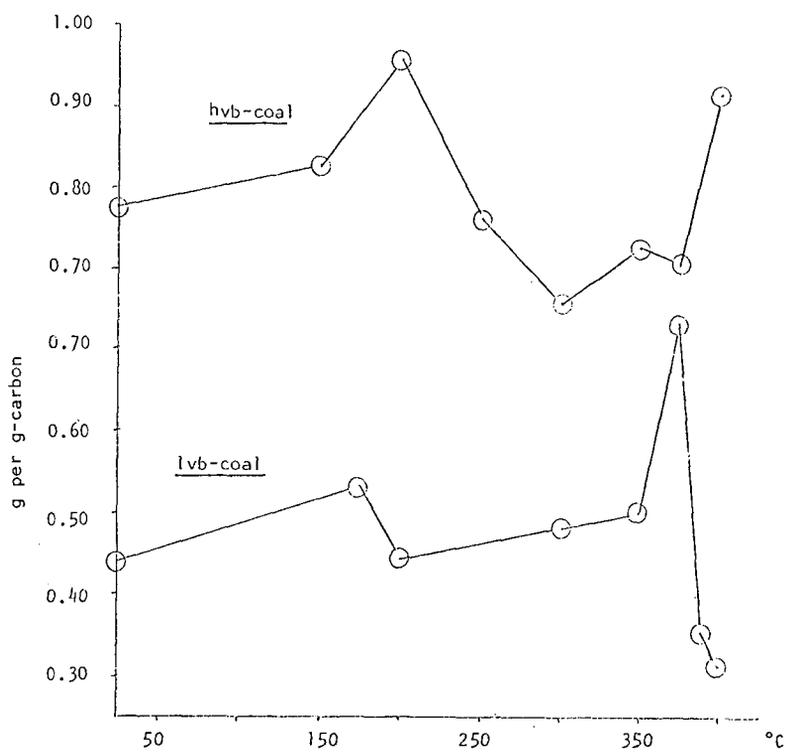   Mo. Wt. >600

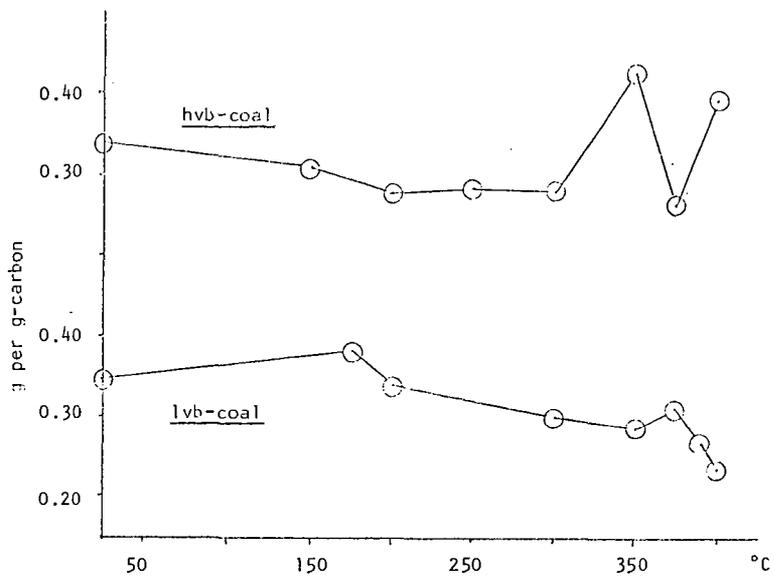Fig. 4. Yield of 'complex acids' as methyl esters
Mol. Wt. <600

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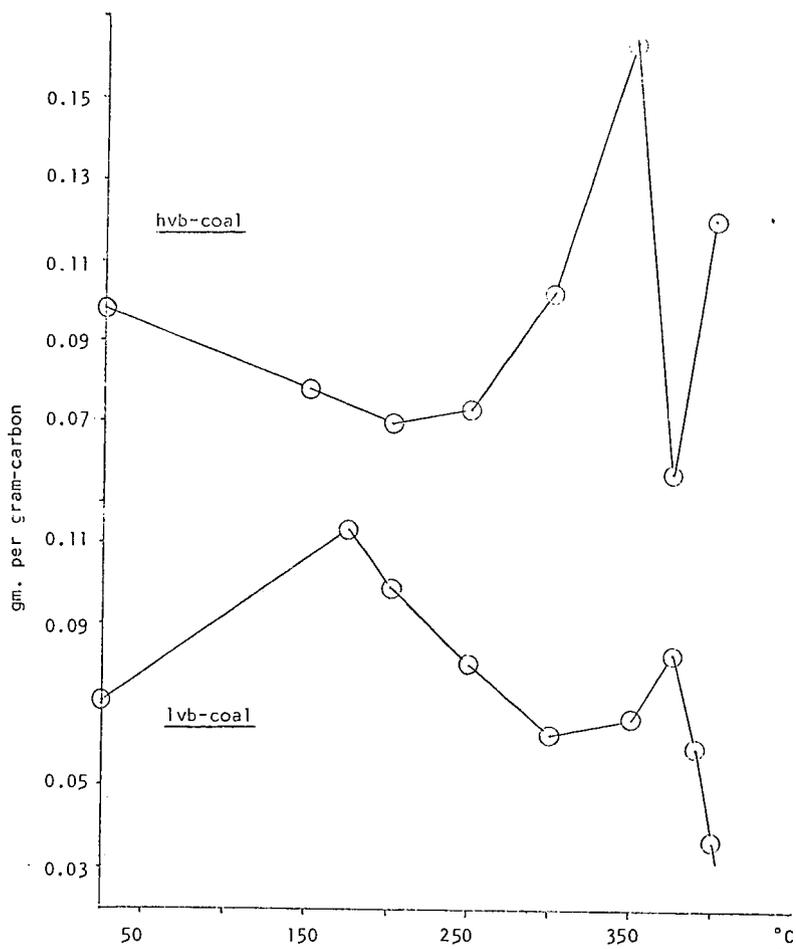Fig. 5 Yield of 'simple acids' as methyl esters.
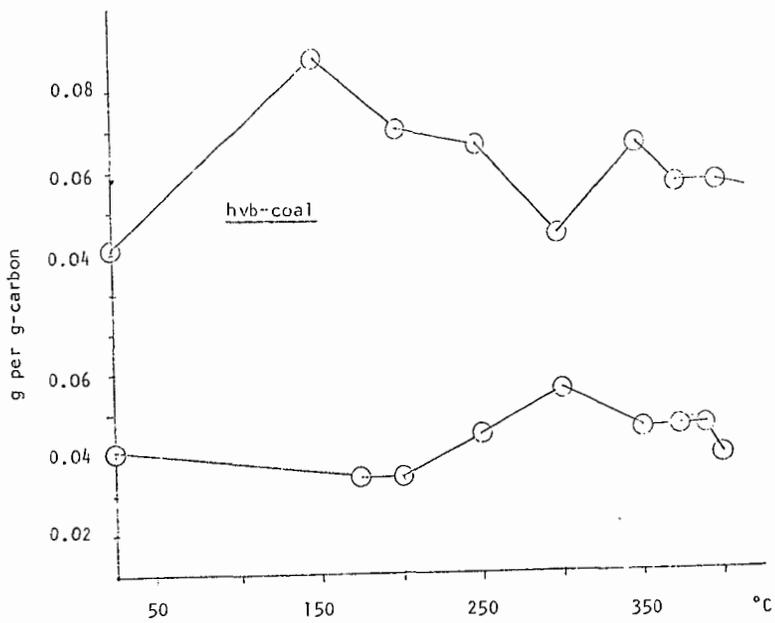
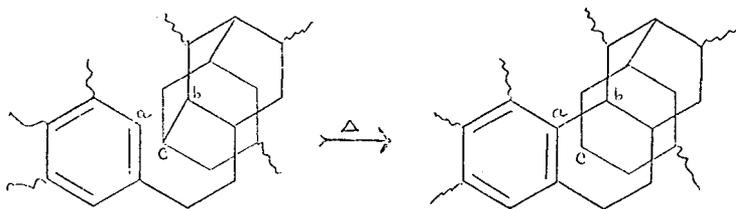Fig. 6 Combined yield of penta- and hexa-carboxyl benzenes.
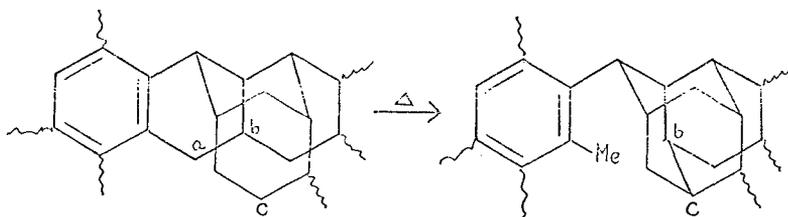
Fig. 7 Combined yield of tri- and tetra-carboxyl toluenes

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Scheme 1

Scheme 2

Fig. 8 Possible isomerization path.

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