

Enhancement of char reactivity by rapid heating of precursor coal

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Char reactivity is generally higher the (a) lower the rank of the precursor coal^{1,2}, (b) lower the temperature to which the char has been taken prior to reaction^{1,3}, (c) shorter the soak time at maximum heat treatment temperature (HTT)³, and (d) smaller the char particle size². We have now found another variable which can affect subsequent char reactivity, that is the heating rate to maximum HTT.

Chars were produced from a 70 × 100 U.S. mesh North Dakota lignite having the following ASTM analysis: ash (dry), 7.3%; VM (daf), 47.1%; and fixed carbon (daf), 52.9%. Chars were prepared by heating the lignite in nitrogen to maximum temperature either in a fluidized bed at 10°C/min or in a laminar-flow unit at about 8 × 10³°C/s⁴. In both cases, soak time at maximum temperature was under 1 s.

Subsequently, char reactivity in 0.1 MPa of air was measured at 500°C in a TGA apparatus as previously described¹. The char sample was heated in the TGA unit at 10°C/min to 500°C in N₂ and soaked for 15 min prior to studying reactivity. Reactivity was expressed as

$$R_T = \frac{1}{W} \frac{dW}{dt}$$

where R_T = reactivity (g h⁻¹ g⁻¹); W = starting weight of char on a dry-ash-free basis (g); and dW/dt = maximum rate of reaction (g h⁻¹). In a number of previous studies, it has been shown that reactivity measurements were reproducible to within ±3% at the 95% confidence level.

Table 1 presents the results. Weight losses upon heat treatment, based on the weight of dried (110°C) starting lignite, are shown. The sample heated to 800°C at 8 × 10³°C/s had a weight loss of only 13.0%, but subsequent heating in the TGA unit prior to reaction with air resulted in an additional weight loss of 22.8%. Therefore, the total weight loss for this sample was 35.8%. The other samples underwent negligible weight loss in N₂ during heat-up in the TGA unit to reaction temperature.

Rapid heating to 800°C yielded a char having a subsequent reactivity almost twice that of the char produced by slow heating to 800°C and a reactivity also greater than that of

the char produced by slow heating to only 500°C. Rapid heating to 800°C of a char which was previously slowly heated to 500°C also produced a substantial increase in reactivity. Even rapid heating to 800°C of a char which was previously slowly heated to 800°C resulted in some enhancement of reactivity. This latter effect was also found for other chars produced from sub-bituminous and HV bituminous coals³.

High char reactivity can be related to such parameters as: (i) high concentration of heteroatoms in the char; (ii) high concentration of active carbon sites; (iii) good accessibility by gaseous reactants to active sites; and (iv) high catalytic activity of inorganic impurities to promote carbon gasification. Each of these factors can be considered briefly in the context of the present studies.

Consider (i). A high concentration of heteroatoms, particularly hydrogen and oxygen, can promote a high reactivity. That is, thermal decomposition of functional groups containing these heteroatoms during the gasification process, as CO₂, CO, and H₂, produces nascent carbon sites which are highly active to subsequent gasification⁵. However, data in Table 1 show a similar weight loss upon heat treatment. The data do not suggest that the concentrations of heteroatoms on the chars which had been produced, at least in part, by rapid heating were significantly higher.

Consider (ii). It is generally recognized in crystal-growth processes that the more rapid the heating to and cooling from maximum temperature the more chaotic is growth. Resulting crystallite size is smaller and the crystallites contain, on average, more defects. Thus, rapid heating of coals and rapid cooling of the product could be expected to yield a higher concentration of active carbon sites in chars. Qualitative observations that the chars produced by rapid heating are more active to oxygen chemisorption at room temperature than those produced by slow heating support this possibility, but quantitative measurements have not as yet been made.

Consider (iii). If reactivity is to be maximized, there must be good accessibility of the reactant gas to the active sites. An estimate of relative accessibility can be obtained by determining specific surface areas of the chars from gas-adsorption data. Measurements were made in N₂ (77 K) and CO₂ (298 K) on the chars slowly and rapidly heated to 800°C prior to putting them into the TGA unit. Chars were outgassed at 500°C prior to making surface-area measurements. The char produced by slow heating had N₂ and CO₂ surface areas of 106 and 511 m²/g (daf basis); the char produced by rapid heating had N₂ and CO₂ surface areas of 157 and 646 m²/g. Both chars showed molecular sieving, but the char produced by rapid heating had higher surface areas. Thus, greater accessibility of reactant to the active sites of this char would be expected.

Table 1 Char reactivity following different heat treatments

Heat treatments	Weight loss on heat treatment (% dry basis)	R_T (g h ⁻¹ g ⁻¹)
10°C/min to 500°C	37.3	3.85
10°C/min to 800°C	43.8	2.79
8 × 10 ³ °C/s to 800°C	13.0, (22.8)	5.17
10°C/min to 800°C followed by 8 × 10 ³ °C/s to 800°C	≈43.8	3.10
10°C/min to 500°C followed by 8 × 10 ³ °C/s to 800°C	≈37.3	4.89

Consider (iv). One of the major reasons why the reactivity of lignite chars is high is that they are produced from coals having a high concentration of calcium associated with carboxyl groups. Upon heat treatment, the carboxyl groups decompose, producing CO₂ and leaving highly dispersed calcium behind. Its specific catalytic activity for promoting carbon gasification is expected to be higher the higher its degree of dispersion and the lower its crystallinity. Definitive results are not yet available which show whether rapid heating does maximize these parameters and, hence, catalytic activity.

In conclusion, it is intriguing that even rapid heating of a char following its production by slow heating of precursor coal leads to enhanced reactivity. It is as if 'thermal shock' of the char resulting from rapid heating and/or cooling leads to enhancement in parameters (ii), (iii) and/or (iv).

Reflectance of burnt coals

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The interrelation between the reflectance and chemical properties of coals heated in the absence of oxygen (i.e. of carbonized or thermally metamorphosed coals) is known^{1,2}. Since no comparable results were available on coals heated in the presence of oxygen, the present authors have studied reflectance and chemical composition of burnt coals, i.e. coals heated in the presence of oxygen. The purpose of the present note is to describe this relation.

Reflectances in oil were determined by the method previously described^{1,3} on samples of burnt outcrop coals from the Jharia coalfield, collected seamwise from the apparent source of fire to the unaffected region. The samples were polished in accordance with the method followed earlier⁴.

In *Figure 1* maximum reflectance in oil has been plotted against carbon content of the burnt coals. For comparison, in this *Figure* the results of maximum reflectance in oil obtained by Chandra and Bond¹ on coals carbonized in the laboratory under normal atmospheric pressure (henceforth referred to as without excess pressure) have also been plotted against the carbon content.

It has been found that the relation between maximum reflectance in oil and carbon content of the burnt coal varies in two stages:

1. *Initial stage*: normally reflectance remains the same but carbon decreases, suggesting oxidation (see sample Nos. 1, 6, 10, 13, 23, 33, 37 in *Figure 1*); this has been observed under careful laboratory conditions⁴, as well as in the natural condition⁵.

When oxidation is accompanied by temperature rise the reflectance increases as the carbon decreases (Sample Nos. 14, 26, 28, 31, 30, 38, 39, in *Figure 1*). This is clearly evident with the samples containing oxidation rims⁶ (*Figure 1*).

Some samples (Nos. 9, 11, 12, 15, 16, 17 and 18) show reflectance values and carbon contents both lower than the corresponding raw coals (*Figure 1*), suggesting probably

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certain conditions of oxidation which have so far not been observed in any laboratory experiment.

2. *Final stage*: reflectance increases with increase in carbon content, and follows a curve that is otherwise obtained by plotting maximum reflectance in oil against carbon content of coals carbonized in the laboratory without excess pressure (*Figure 1*).

In *Figure 2* maximum reflectance in oil has been plotted against hydrogen content. For comparison the maximum reflectance in oil of coals carbonized in the laboratory without excess pressure obtained by Chandra and Bond¹ has also been plotted against hydrogen content. It will be seen that the maximum reflectance in oil of carbonized coals without excess pressure varies with hydrogen content depending on the rank of coal.

There are two separate curves, one for the low-rank coals, Thorne Hazel, C 83.1% (daf) and Ashton Moss Roger, C 84.1% (daf), and the other for high-rank Penrikyber coal, C 91.3% (daf), showing the relation between maximum reflectance in oil and hydrogen content of the coals carbonized in the laboratory without excess pressure. But the burnt coals do not appear to show any generalized relation between the maximum reflectance in oil and the hydrogen content.

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