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Letters to the Editor

Concurrent carbon gasification and carbon deposition in chars

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Polycrystalline chars and cokes contain internal porosity, much of which can be characterized as an aperture—cavity system[1-3]. The apertures are thought to be formed primarily by the approach of basal planes of small adjacent crystallites, the closeness of approach being determined by the frequency and nature of crosslinks between the planar building blocks. The extent of porosity within the cavities is generally associated with the degree of crystallite alignment. As alignment increases, porosity decreases[1].

The size of the apertures in chars, and hence accessible porosity, can be changed dramatically by small amounts of carbon gasification[4] or carbon deposition[5]. That is, chars are molecular-sieve materials, with their aperture sizes broadly similar to those of molecules important in gasification reactions. The exact nature of the molecular sieving is a function of the organic precursor from which the char is produced and the heat-treatment conditions used in the charring process. Small amounts of gasification can remove sufficient carbon atoms from apertures to make large amounts of cavity volume and area accessible. Conversely, small amounts of carbon deposition at apertures as a result of hydrocarbon cracking can make cavities inaccessible to even the smallest molecule, helium.

Obviously an understanding of the nature of the aperture—cavity system in chars and how it changes with heat treatment, volatile-matter loss, gasification, and carbon deposition is necessary in order to be able to optimize gasification rates of chars and to model mathematically gasification processes. This note introduces the concept of concurrent carbon gasification and carbon deposition in chars. We will observe the interdependence of rates of these two processes and how this interdependence can change depending upon the particular char used.

Chars were produced from a Montana lignite (PSOC-91[6]) and Saran (a copolymer of polyvinylidene chloride and polyvinyl chloride[7]) by heating them to 1000°C and soaking for 2 h in N_2. Part of the lignite char was washed with warm 10% (by volume) hydrochloric acid; this reduced ash from 10.9 to 7.2%.

A Fisher TGA unit, Model 442, was used for both gasification and carbon deposition studies. About 3 mg of 40 × 100 U.S. standard mesh char were first heated to 1000°C in flowing N_2 until the sample weight became constant. The sample was then cooled to reaction temperature (900°C) and held for 20 min prior to introducing the desired reaction mixture. Carbon dioxide and steam were used for gasification, methane was used for carbon deposition, and N_2 was the diluent.

Results with mixtures showed effects all the way from the gasification reaction promoting a continuing high rate of carbon deposition from methane, to carbon deposition completely retarding the gasification reaction — even in the same gas mixture but for different chars. Such results are shown in *Figures 1* and *2*. In *Figure 1*, curves (a) and (b) show weight loss and weight gain plots for the acid-washed
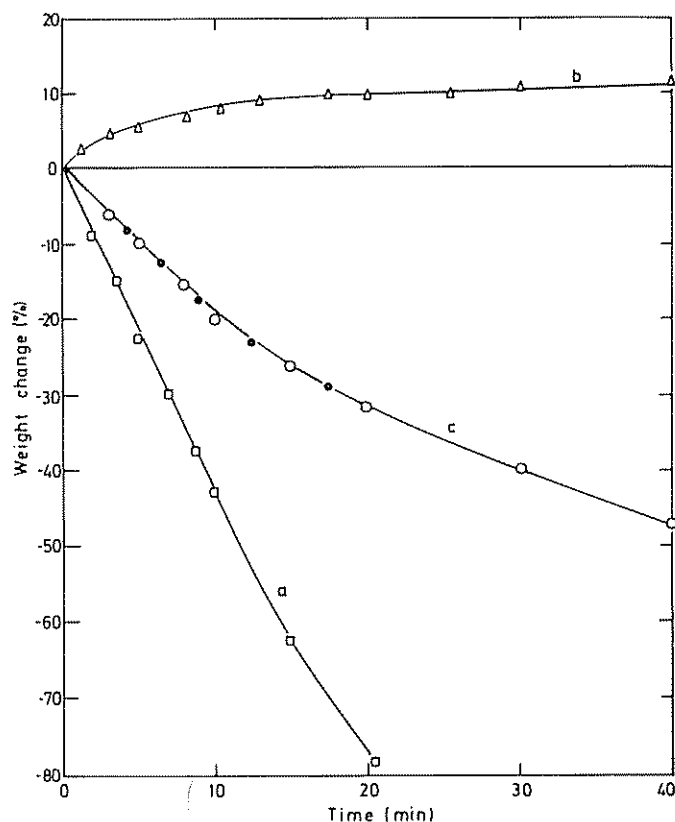
Figure 1 Weight change in the acid-washed lignite char at 900°C in various atmospheres: (a) 30% CO_2; (b) 40% CH_4; (c) 30% CO_2 –40% CH_4. N_2 is the diluent. On curve (c), open points are experimental and closed points are calculated
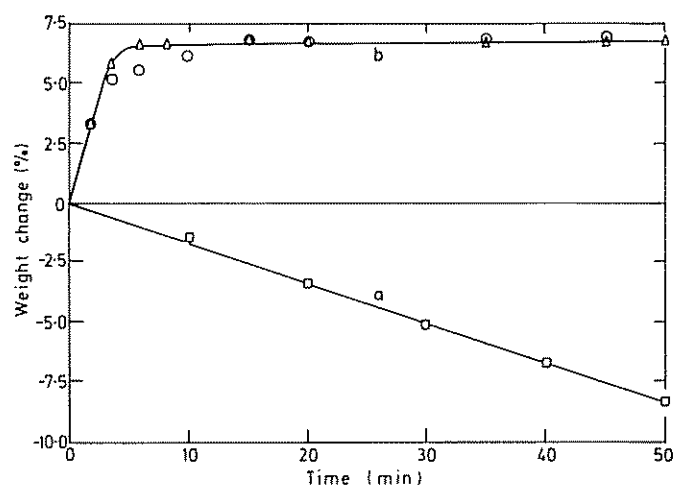
Figure 2 Weight change in the Saran char at 900°C in various atmospheres: (a) 30% CO_2 (□); (b) 40% CH_4 (△) and 30% CO_2—40% CH_4 (○). N_2 is the diluent

lignite char in 30% CO_2–70% N_2 and 40% CH_4–60% N_2 mixtures, respectively. As has been previously discussed[5], carbon deposition in chars from the cracking of methane essentially stops when only a fraction of the total pore volume in the char is filled. This has been attributed to a decrease in aperture size to an extent that methane no longer has access to the porosity within the cavities. However, it is possible in a CO_2–CH_4 mixture that the gasification of carbon atoms deposited from methane at aperture openings is sufficiently rapid that the rate of carbon deposition is not retarded. This is the situation which exists for the results shown in *Figure 1*. That is, curve (c) (open points) shows the experimental carbon weight loss *vs.* time plot for the mixture 30% CO_2–40% CH_4–30% N_2. The closed points on curve (c) were calculated, assuming that the initial rate of carbon deposition from the 40% CH_4–60% N_2 mixture continues throughout the run. That is, the cumulative carbon deposited, as calculated from the initial rate (estimated to be 2.2% weight gain/min), is subtracted from curve (a). Good agreement between the experimental and calculated results is seen.

In *Figure 2*, curves (a) and (b) show weight loss and weight gain plots for the Saran char in 30% CO_2–70% N_2 and 40% CH_4–60% N_2 mixtures, respectively. However, unlike the results shown in *Figure 1*, when the 30% CO_2–40% CH_4–30% N_2 mixture is passed over the char, a net weight gain is found, with the data points very close to that described by curve (b). The reason for this is that, whereas the rates of carbon deposition from methane are similar over the acid-washed lignite and Saran chars, the rate of gasification of the lignite char in CO_2 is considerably higher than that found for the Saran char. Similar results were found for these two chars when steam was substituted for CO_2. These results show the complexity of predicting changes in char weight in the presence of mixed gas systems. Inability to predict is caused by variations in carbon gasification and deposition rates affected by differences in: (1) the configuration of edge carbon atoms terminating crystallite basal planes, i.e. arm-chair and zig-zag[8], (2) the chemical and physical nature of inorganic impurities (catalysts) present[9], (3) extents of inhibition of the reactions by product hydrogen[10,11], and (4) the concentration of nascent sites.

Considering point (4), it is suspected that freshly deposited carbon has a 'super' reactivity to gasification and, conversely, that edge carbon sites newly exposed by gasification have 'super' catalytic activity to hydrocarbon cracking.

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Carbon deposition from methane over minerals

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Studies on carbon deposition from methane over a lignite char have been conducted[1]. Since deposition rates were more rapid over the raw char than the HCl-treated char, it was concluded that catalysis of methane cracking by some inorganic species occurred. Thus, we have studied the cracking of methane over different major minerals found in coals in a TGA unit at 900°C at a total pressure of 0.1 MPa in a flowing CH_4–N_2 mixture. The partial pressure of methane was 6.5×10^{-3} MPa. Prior to studying methane cracking at 900°C, the mineral sample (about 10 mg ground to –44 μm) was heated up in N_2 at 20°C/min and held at 900°C for 30 min. *Table 1* lists the minerals studied and reactions which they undergo upon heating in N_2 to 900°C[2].

Of all the minerals studied, only siderite and calcite were found to be precursors of catalysts for the cracking of methane. Gypsum was found to react with methane giving predominantly CaS and small amounts of $CaSO_4$ and CaO. No surface deposition of carbon was observed. In both N_2 and methane at 900°C, pyrite lost sulphur and was converted to triolite (FeS), but there was no evidence of either reduction of triolite to iron or of carbon formation. The cases of siderite and calcite can be considered in more detail.