

THE EFFECT OF NATURAL COAL IMPURITIES ON CARBON GASIFICATION

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In an earlier study, steam-gasification kinetics of 6 chars, prepared from coals of U.S. and German origin, and pure graphite were compared. The gasification was followed gravimetrically in a recirculation system at a water pressure of 2.67 kPa. Rates were evaluated per unit surface area, obtained in situ, from carbon dioxide adsorption at the temperature of dry ice. Five of the six chars yielded specific gasification rates less than a factor of 4 higher (at 850 C) than that of pure graphite. The sixth char, prepared from a German lignite, Braunkohle (BK), yielded a 10-fold rate increase over graphite. At the same time, the activation energy of gasification of this char was lower (59 kcal/mol) than the corresponding values of the other chars (65-82 kcal/mol). It was of interest to study with the same experimental arrangement, whether the reactivity of BK char was higher due to a true catalytic action of its impurities, or to an increase in the number of gasification sites.

Three approaches were selected to study the effects of natural coal impurities on the steam gasification of chars: (a) addition of coal ash to graphite, (b) addition of ash to a less reactive coal, and (c) removal of noncarbonaceous matter from the lignite by acid-leaching.

Metals, such as Fe, Co, Ni, Ru, Rh, Pd and Pt can increase steam gasification of graphite by several orders of magnitude. The results obtained for 3% of BK ash in graphite are shown in the table below. Rates, taken at 850 C, remain constant up to almost 80% burn-off. A 12- to 16-fold enhancement is observed compared to pure graphite, as the table shows, accompanied by a decrease in activation energy. Addition of ash from a Pittsburgh seam coal (PSC) to graphite did not cause such changes.

Nickel and other catalysts, which are quite active in graphite gasification, influence the reaction of chars much less. Furthermore, activity in chars is often lost quickly, while it persists in graphite. These discrepancies can be explained by structural differences. Thus, electron micrographs show extensive channel formations in graphite, indicating preservation of contact between metal particles and graphite surface, while

contact loss in chars can be deduced from the agglomeration and isolation of catalyst particles in craters of the char structure. In addition, the much larger surface areas of chars require a 100-fold increase in catalyst concentration per unit weight, compared to graphite, to achieve the same ratio of catalyst weight to carbon-surface area.

T A B L E

Activation Energies and Specific Gasification Rates

Burn-off %	BET Area m ² /g	Activ. Energy kcal/mol	Rate at 850°C μg/(m ² ·min)
A. Pure SPL-Graphite			
13	3.6	80.5	0.3
B. Graphite + 3% BK Ash			
0	2.5	61.9	4.4
14	3.4	60.1	4.8
28	4.3	61.9	4.3
40	5.3	61.4	4.5
80	7.9	64.5	3.6
C. PSC Char, untreated			
19	407	66.3	0.7
D. BK Char, untreated			
24	436	59.5	4.7
E. PSC + 3% BK Ash			
0	318	58.7	4.3
17	293	64.7	2.1
48	276	72.8	1.9
F. BK, leached by HF+HCl+HNO ₃			
25	625	67.1	1.5
G. BK, leached by HF+HCl			
24	592	58.3	2.0
H. BK, leached by HNO ₃			
30	629	59.6	2.1

With these facts in mind, the effect of 3% BK ash, added to PSC, a coal of low reactivity, was examined. For comparable surface areas and stages of burn-off, the specific gasification rate of BK char exceeds that of PSC char more than 6-fold. Of the two chars, BK shows the lower apparent activation energy. Addition of 3% BK ash to PSC produced a marked enhancement in the rate of char gasification. The rate decrease with burn-off indicates some contact loss between the active ash particles and the char surface. At 17% burn-off, the kinetic data fall about halfway between the corresponding values of the untreated chars of BK and PSC. PSC char containing nickel or potassium carbonate showed a much steeper loss of catalytic activity. It is remarkable that the sample pellet containing BK ash could be reacted completely while suspended by a quartz-glass fiber; in fact, the surface of the remaining ash could be measured in situ. These results suggest that the added ash has the ability to preserve contact with the carbon surface, possibly by incipient melting and wetting, or by redistribution through the vapor phase.

Analyses of the ashes of BK and PSC by x-ray fluorescence showed the same elements to be present, the main elements being Fe, Ca, Ti, Si, Al, K and S. However, there was a distinct difference in the distribution of these elements. Quantitatively, one would have expected an advantage of the higher ash content of PSC (6%) over that of BK (4%). When BK was

leached by a mixture of HNO_3 , HF and HCl, elements found in the solution by atomic adsorption were Fe, Ca, Ti, Si, Al, B and Mg.

A comparison of the gasification rates of BK char, after the acid leachings, is listed in the table. The simultaneous leaching by the three acids caused a decrease of the specific rate by a factor of three, and an increase in the apparent activation energy. It is not known, whether the higher activation energy results from a loss in catalytic action, or from an increase in pore size, which appears possible in view of the increased surface area. The two other leachings caused smaller decreases in the reaction rates, as shown in the table. Differences are also noticeable in the micrographs of leached and unleached BK char.

A parallel study was performed with a lignite of North Dakota origin; it was found to be even more reactive than BK when exposed to steam. The kinetic results obtained from the leaching and ash-impregnation experiments on the two lignites, which show distinct similarities, are compared in considerable detail.

Ash transfer from a reactive to an unreactive coal is an interesting possibility for improving gasification of a particular coal, or for equalizing gasification characteristics when blending coals of different sources.