

STAGES IN THE COALIFICATION SEQUENCE REFLECTED IN OXIDATION REACTIVITIES

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(Received 18 January 2002; Accepted 5 February 2002)

ABSTRACT

Materials representing the transition which occurs during coal formation from vegetation are examined for intrinsic reactivity in terms of heat release rate. Only faint trends emerge from the limited data available. These are however fully discussed and it is hoped that a wider discussion of this idea might be engendered.

1. INTRODUCTION

In the coalification sequence, the time scale of which is tens or hundreds of millions of years, the biochemical stage concludes with the conversion of cellulose to humic acids, and this is followed by the geochemical stage. Anthracite is the coal of highest rank. It is important not to confuse the concepts of 'rank' and 'type'. Rank is a measure of the maturity of a coal which is why, as already stated, anthracite is the coal of highest rank. Coal type depends upon the nature of the initial vegetation deposit, reflected in the 'macerals' – the organic counterpart of 'minerals' – of which the coal is composed. The three maceral groups are vitrinite, exinite and inertinite, there being many individual macerals within the groups, the classification being to some extent arbitrary (see comment in the final section).

The term maceral was coined some 85 years ago by Dr. Marie Stopes, who laid the foundations of the branch of science now known as coal petrography. Microscopic examination, using plane polarised light, of sections of coal for their maceral composition is standard procedure in coal science laboratories around the world. However, with higher rank coals such as anthracites, the significance of 'type' is reduced since the various macerals start to approach the same composition at

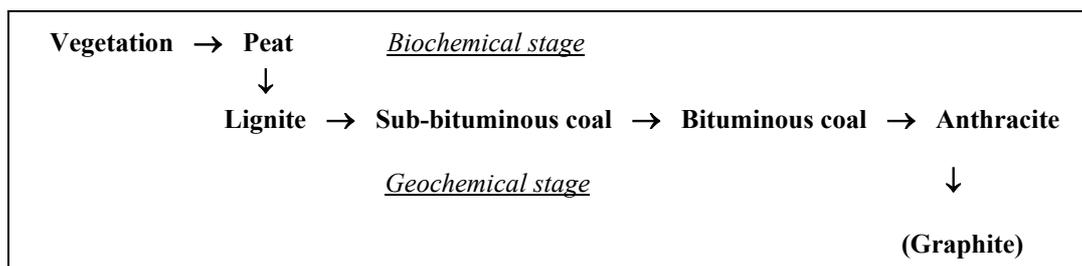
advanced stages of coalification. The ultimate in coalification, attained by only very few deposits in the world, is formation of elemental carbon as graphite, and clearly the concept of macerals has no application to this.

Coals of different rank tend to display a negative correlation between rank and intrinsic reactivity towards combustion, making anthracites less reactive than, for example, lignites. In the present paper, some original results from microcalorimetric work on an anthracite will be reported and compared with those from materials representing a lower degree of coalification. In this way, a pattern of reactivities according to rank might be expected to emerge. The coalification series can be summarised [1] according to Fig. 1.

2. EXPERIMENTAL

The anthracite was from a UK deposit and microcalorimetric measurements performed to assess its heat release rate at different temperatures in exactly the way described previously for the other materials data for which, previously reported, will be used herein. The results for anthracite will in due course be interpreted according to the principles of chemical kinetics [2].

Fig. 1: Outline of the coalification sequence



3. Results

Each trace from the microcalorimeter showed steady behaviour only for time of the order of an hour before dropping. This was determined four times at 60°C, and the results are shown in Table 1.

The considerable spread is no doubt due to small composition variations between successive samples. In Table 2, materials previously studied are compared with the anthracite in terms of their heat release rate at 60°C or the closest temperature to that for which information is available. In the table, the materials are arranged in an order which mirrors the coalification sequence.

4. DISCUSSION

In Table 2, the range of heat release rates across the materials representing the coalification sequence is from zero up to quantities of the order of 1 W kg⁻¹. The chemical changes occurring in coalification are, in the biochemical stage, conversion of cellulose to humic acids. The significance of the statement of the results for peat that the samples had previously been examined at lower temperatures is that there might have been some deactivation during such examination.

Table 1: Heat release rates for anthracite at 60°C

Weight of anthracite / mg	Peak heat release rate $q / \mu\text{W}$	Peak heat release rate per unit mass $q / \text{mW kg}^{-1}$
220	12.4	56
140	8.5	61
70	5.7	81
235	10.6	45

$$q (\text{anthracite}) = (61 \pm 20) \text{ mW kg}^{-1}$$

Table 2: Heat release rates for materials representing different degrees of coalification

Material and quantity	Reference	Heat release rate q at the temperature specified / W kg ⁻¹
<u>Forest litter</u> 90 mg representing vegetation, which is the starting material in coal formation.	3	0.13 at 58°C
<u>Sugar cane residue</u> 100 mg also representative of vegetation.	4	0.093 at 60°C
<u>Briquetted peat</u> (a) 950 mg (b) 350 mg	5	(a) 0.066 at 60°C, the sample having previously been examined in the microcalorimeter at lower temperatures. (b) 0.034 at 64°C, the sample having previously been examined in the microcalorimeter at lower temperatures.
<u>German lignite</u> three 60 mg samples	6	0.25, 0.65 and 1.04 at 55°C
<u>Australian lignite</u> 65 mg	7	0.92 at 60°C
<u>UK bituminous coal</u> 650 mg	8	0.030 at 58°C
<u>UK anthracite</u> Several masses, mean heat release rate given (see above)	Present work	0.061 at 60°C
<u>Graphite</u> 1360 mg	9	Zero at 60°C and higher

There remain two marked observations which, even in view of the very limited number of data, can at least tentatively be reported. There is change of half to one orders of magnitude in heat release rates during the first step of the geochemical stage of coalification, that is, from peat to lignite. From there, there is progressive reduction to zero for graphite. As the geochemical stage of coalification takes its course, the oxygen content decreases, the carbon content increases and porosity decreases. Early in the geochemical stage, the interplay of these factors is such as to maximise reactivity. In terms of the decrease of reactivity with increasing carbon content, it is relevant to invoke the well-known fact of basic combustion chemistry that oxygenated hydrocarbons are often more reactive than the parent unsubstituted hydrocarbon; for example, acetaldehyde (CH_3CHO) is, under many reacting conditions applied in laboratory studies, much more reactive than ethane (C_2H_6).

5. CONCLUDING REMARKS

In some respects, this paper has done little more than pose a question: are the changes which occur during coalification traceable in terms of intrinsic reactivities to oxygen of deposits of various maturities? Only a few data have been presented in support of this novel idea, though these enable provisional conclusions to be drawn.

The changes during coalification are traceable in terms of chemical and, more importantly, petrographic analysis. An obvious direction in which to extend these ideas is for coals of similar petrographic composition but different rank to be so examined. This would however be a far from simple project to plan, let alone to execute and interpret. This is because macerals, unlike their inorganic counterparts minerals, have no precise composition. Moreover, even the definition of a particular maceral is not clear-cut, and definitions and criteria are subject to constant review. There is also the possible obscuring of the effects of chemical and petrographic changes by attenuated porosity with increasing maturity of a deposit. Nevertheless the idea of correlating reactivity with degree of coalification has been set out and discussed herein and the authors would welcome comments from readers.

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