

## COAL CHARACTERISATION BY THERMAL ANALYSIS

ALEXANDRA DE KORÁNYI

*British Gas Corporation, London Research Station, Michael Road,  
London SW6 2AD (Gt. Britain)*

### ABSTRACT

Most coal research is aimed either directly or indirectly at gasification, pyrolysis, combustion or liquefaction. The 22 papers presented at the 8th ICTA on coal included a wide range of coal or carbon topics. Among these were examination of coal composition by proximate analysis, as well as low-temperature ashing and multiple atmosphere differential thermal analysis, thermogravimetry and differential thermogravimetry for the study of mineral matter content. Devolatilisation products were examined and the effects of pre-treatment on coal thermal degradation. Investigation of new materials included thermally exfoliated graphite made from graphite intercalation compounds, and materials made from cellulose derivatives. New methods of thermal analysis used by some authors included thermomagnometry and evolved gas analysis, emanation thermal analysis and differential scanning calorimetry. Among the papers presented were a few, only, in the area of coal studies and the usefulness of thermal analysis and thermogravimetric analysis techniques in this area could be expanded greatly.

### INTRODUCTION

As a result of the depletion of oil and gas resources occurring throughout the world in recent years, there has been renewed interest in more efficient use of the vast reserves of coal that exist worldwide.

Most of coal research is aimed directly or indirectly at one of the four main areas of coal utilisation; pyrolysis, gasification, combustion or liquefaction. Experimental techniques to define the properties of coal and carbons quantitatively are still being developed. Thermal methods of analysis have improved greatly in recent years, and this process is on-going. The coupling of computers with instruments for control and data processing has also made a significant contribution to coal research.

### COAL CHARACTERISATION

Characterisation of the composition of coals and coal chars is of great importance for their final use. Coals contain mostly carbon, together with

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ash or mineral matter, as well as tars, hydrogen and volatiles. Thermogravimetry (TG) and thermal analysis (TA) are used for proximate analysis of coals reducing the analysis time to 1 h from 24 h by previous methods. Thermal analysis can be used as an analytical tool for characterising coals and chars as seen in the paper of Markova et al. [1] which showed the effect on the analysis of different petrographic and chemical compositions of various types of coal. Proximate analysis was used also in Hill et al.'s [2] paper comparing Australian brown coals with European lignites and American anthracites.

Thermal analysis (TA) and thermogravimetric analysis (TGA) can be used as a fingerprint to examine coal-burning profiles by obtaining activation energies. These activation energies can be used to predict the temperature which samples reach in a gasifier, and can be employed in boiler design. They can be used to determine pyrite ( $\text{FeS}_2$ ) content of coals. Thermomagnetometry, which will measure the magnetic attraction of iron in pyrite, when combined with TG, is a new and useful method of analysis. However, the method will give ambiguous results when siderite ( $\text{FeCO}_3$ ) is also present in coal. In Warne et al.'s paper [3], another thermoanalytical method for pyrite determination (evolved gas analysis) was used.  $\text{SO}_2$  evolved from pyrite on heating in an oxidising atmosphere was analysed directly with non-dispersive IR detectors.

Low-temperature ashing of coals (LTA) removes the organic carbon from coal by heating the coal in an  $\text{O}_2$  plasma below  $250^\circ\text{C}$ , prior to thermal analysis. Thermal properties of minerals will then determine how a coal sample is pre-treated before analysis. High-temperature DTA, TG and DTG offer direct approaches to the study of mineral matter in coals, not only as a diagnostic and analytical tool, but in establishing the behaviour of mineral matter on heating in different atmospheres. These techniques were used in Earnest et al.'s [4] paper to study the LTA components of some Kentucky and Illinois coals. These samples were analysed by thermal methods in different atmospheres to obtain information on the behaviour of mineral matter. Differences in DTA patterns for SW Illinois coal in dynamic air and  $\text{CO}_2$  can be seen in Fig. 1.

Large amounts of ash produced from power stations can present economic and ecological problems. The use the ash is put to will depend on its properties and composition. Hodzic and Pasic's [5] paper showed the necessity of monitoring different electrofilter ash layers by DTG and TG. Different layers had different temperature characteristics.

Mineral matter present in coals can act as a catalyst to speed up or retard a reaction in any of the coal utilisation processes. In the liquefaction process, the rate of liquefaction increases directly with the concentration of mineral matter, depending upon the composition. TG and DTA were used in Aleksic and Kosanic's paper [6]. These authors studied lignite and brown coals in different atmospheres in order to assess their chemical properties

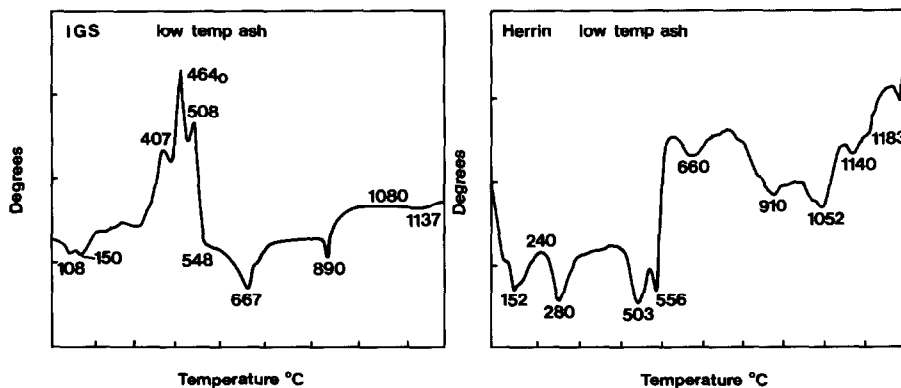


Fig. 1. DTA curves for SW Illinois coal in dynamic air (left) and  $\text{CO}_2$  (right) atmospheres.

and to determine their reactivity as a source of liquid fuels produced by catalytic hydrogenation.

Among the major components of mineral matter found in coal are the clay minerals and carbonates which exhibit strong endothermic decompositions. The effect of addition of alkaline carbonate on demineralised lignite chars obtained from coal at different temperatures was studied by Rustchev and Atanassov [7].

Kettrup and Ohrbach [8] used combined thermal analysis and mass spectrometry to investigate coal samples as an energy resource and to study their devolatilisation products with regard to environmental pollution. PVC and PU foam were examined too, for their degradation mechanisms.

The effect of different factors and treatments on the thermal degradation of coals by TG was studied by Smutkina et al. [9]. Figure 2 shows the

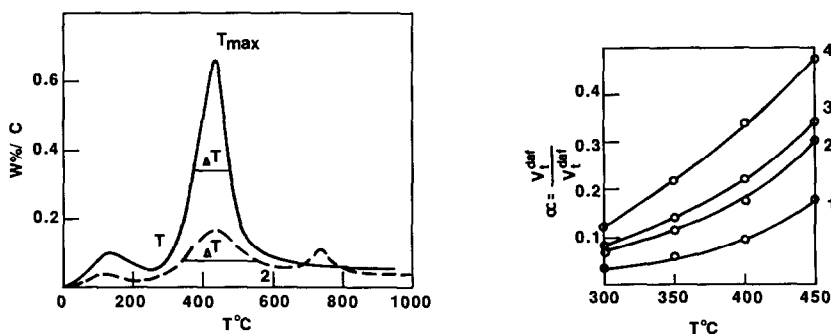
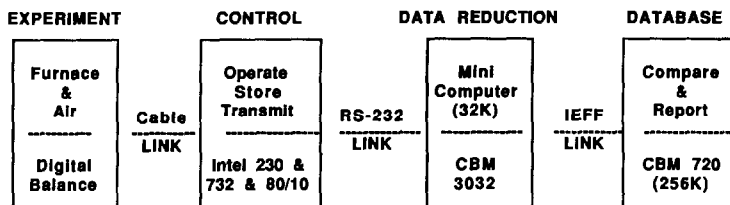


Fig. 2. Curve shape of mass loss rate for (—) strong hydrogenating coals and (- - -) weak hydrogenating coals.

Fig. 3. Degree of decomposition of coal vs. temperature with certain additives: (1) initial coal, (2) 1%  $\text{Fe}^{3+}$  and 0.2%  $\text{Mo}^{2+}$ , (3)  $\text{SnCl}_2$ , (4)  $\text{PdCl}_2$ .



The furnace has a temperature range from 20 to 1000°C

Fig. 4. Data bank for comparison of coals.

difference between strong and weak hydrogenating coals. Figure 3 shows the effect of catalytic additives.

Coal combustion, in comparison to gasification, presents some unique properties which derive from the high rapidity and exothermicity of the combustion reaction. Of special importance to combustion is the effect of sample size and thermal annealing, and consequently, the role of diffusion. Saayman [10] developed DTG equipment, together with computerised data reduction, in order to express all parameters of coals in terms of their thermal dissociation features. Results were then, and are now, being used to select standard reference information from other coals in a data bank for comparison and assessment of the combustion characteristics (Fig. 4).

Sulphur can be a problem in the process of fluidised bed coal combustion for power generation. However, the addition of limestone will reduce the amount of sulphur emitted. TG/DTA was used by Mikhail [11] to monitor the efficiency of coal combustion processes to which limestone was added.

## CARBON MATERIALS

Thermodynamics, reaction rates and activation energies, as well as heat capacities and thermal expansion, can be found using DTA and TG. Thermally exfoliated graphite (TEG) is a new type of graphite, the structure of which defines its unique properties for the production of new materials employed for specific purposes. The heat capacity and thermal expansion of a wide range of new graphite and graphitised materials were examined by Kurnevich et al. [12]. The results differed from those obtained from natural graphites, and the latter also produced differing results, depending on the deposit origin. These types of data are lacking, and hence properties must be measured for each graphite material, whether natural or artificial.

In order to show the correlation between TEG properties and those of the raw materials for TEG production, thermal analysis was carried out on graphite bisulphates and their pyrolysis products by Skoropanov et al. [13].

TEG powders with a wide range of properties were obtained. These were dependent on the sequence of carbon and intercalation component layer alternation, and the GIC–H<sub>2</sub>SO<sub>4</sub> pyrolysis process. Skoropanov et al. [14] also investigated the behaviour of GIC (graphite intercalation compounds) with CuCl<sub>2</sub>; they found that results depended on the thermal and basic compound pre-history.

Graphite intercalation compounds with alkali metal fluorination products can be used as catalysts for industrial organic synthesis reactions. Alfer et al. [15] studied such products of a GIC made from graphite and caesium fluoride using TG and DTA.

Cellulose is another material with many potential uses which can be usefully studied by TA methods. Uryash et al. [16] studied the heat capacity and physical transitions of cellulose, its derivatives and their mixtures with plasticisers between 4 and 600 K; diagrams of the physical states of the systems were constructed.

The influence of fire retardants on the formation and development of polyconjugated systems in cellulose was studied by Skripchenko et al. [17]. The formation of such “polyconjugated blocks” and their dimensions increased with temperature. The addition of phosphoric acid accelerated cellulose dehydration and increased the thermal stability of the intermediate structure, thereby influencing the formation of such polyconjugated systems.

The factors affecting the thermal stability of modified polymers are important. Simkovic et al. [18] studied the thermooxidation of TMAHP–cellulose by DTA and a sequence of samples was made according to their increasing thermooxidative effect. Likewise, Kogerman [19] investigated the thermal destruction of some cellulose derivatives and the influence of modifiers on the thermal stability. The effect of doping on the thermodestruction of regenerated cellulose was the theme of the paper of Kurnevich et al. [20]. These authors used different amounts of NH<sub>4</sub>Cl as the doping agents and described the mechanisms involved.

## FUNDAMENTAL RESEARCH

Only relatively recently has research been attempted on specific surface area, active site concentration or sample impurities. These studies are important in understanding the kinetics of coal char gasification and combustion, and thus, carefully measured intrinsic data are important. The pore structure will determine the surface area accessible to reactants; and active sites, where reactions occur in coal chars, are found within the network of micropores. Among others, Walker [21] recognised the importance of active surface areas (ASA) for gasification. Methods of measuring ASA are being developed [22]. Study of the development of pore structure, to its optimum for gasification, during coal pyrolysis, was the theme of de Korányi and

Balek's paper [23]. They studied bituminous coals. A new technique, emanation thermal analysis (ETA), was also used, together with DTG and porosity measurements to give an added dimension. Such novel techniques, in conjunction with the use of TA and TG and other methods, add to the general understanding of fundamental processes.

Even though gas-carbon reactions have been a part of our industrial economy for decades, a fundamental understanding of the reaction mechanisms and kinetics involved has lagged far behind their practical use. Most papers at this Conference showed the use of TA as an analytical tool. However, much research is going on in the overall area of kinetics and reactivity of char-gas reactions; and an understanding of the interaction between gas and solid is important. Mechanisms have been developed to describe these interactions, such as the shrinking core model [24] and the one-dimensional coal gasification or DICOG model [25], which put theories on the solid basis of a mathematical model.

Models to describe mass transport and the heterogeneous chemistry which occurs during coal pyrolysis and gasification are being developed. One of the most complete models on microscopic pore diffusion is the pore tree structure model [26] developed recently by Simons. Such models reflect in detail the essence of overall char reactions.

Differential scanning calorimetry (DSC) is a new thermoanalytical method which was used by Kunihsa and Ogawa [27] to study acid hydrolysis of cellulose using dilute  $H_2SO_4$ . DSC has the potential for measuring the reactivity of coal chars. More work needs to be done in the area of reactivity of different coal chars with  $O_2$ , steam and  $H_2$ , as well as in high-pressure gasification where reactivity data are lacking. Heterogeneous kinetic studies need broadening and new experimental techniques need to be developed. More and more work is being done, also, in the area of the catalytic effect of inorganic impurities on reactivity.

## CONCLUSIONS

The potential use of thermoanalytical and thermogravimetric techniques in the field of coal characterisation and reaction is enormous. At this Conference, we have seen only a very small part of the usefulness of these methods in the area of coal studies. However, with further work and increased understanding of coal utilisation, the vast resources of this fossil fuel can be used with greater efficiency to the benefit of mankind.

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