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FOSSIL FUELS: AN OVERVIEW OF TRENDS, METHODS AND APPLICATIONS OF THERMAL ANALYSIS *

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ABSTRACT

Over the last two decades, thermal analysis (TA) has passed through phases of full recognition and consolidation to rapid expansion owing to advances in several directions, i.e. the establishment by ICTA of standard materials, increased refinement and wider application of established TA methods, the development of new methods, and the invaluable regular reviews of the whole field of TA established by C.B. Murphy. New techniques have been evolved (e.g. "variable atmosphere thermal analysis"), and techniques have been coupled together to give synchronous determinations of several parameters under identical conditions. A resurgence of applications to solid fossil fuels has resulted.

INTRODUCTION

With world energy consumption increasing, petroleum resources and reserves limited, and nuclear sources strongly questioned, the emphasis of fuel research has turned increasingly to coal and potentially oil shale [1]. These solid fossil fuels occur with enormous reserves, have wide geographic distribution, and are readily mined, distributed and utilized. Further, potential environmental damage on accidental spillage of these solid materials is minimal, and easily contained or recovered.

Such solid hydrocarbon-rich fuels are composed of two fundamentally very different groups of components: the organic (hydrocarbon) macerals, and the inorganic minerals. The macerals represent the plant materials in the original peat swamps, while the minerals were washed or blown in from the adjacent land or precipitated from solution in the peat swamp.

The type, composition, quality and thermal decomposition characteristics of the various components control the behaviour, utilization and value of these fuels. On the positive side, they determine calorific value, volatile

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matter yield, petrochemical and coking potential, fly ash yields and compositions, together with washability (beneficiation) potential. Unwanted products are ash, slag, washery rejects, SO_x, NO_x and CO_2. The chemical and physical stability behaviour and toxicity of these solids have considerable negative cost impact in view of the huge quantities produced, i.e. the solid products represent a major physical disposal problem (transport and location), run-off water may be toxic, while gaseous products contribute to acid rain and the greenhouse effect. As coal (and oil shale) uses involve heating, thermal analysis (TA) methods are eminently suitable for many aspects of fossil fuel research. Often these TA methods are superior, offering a viable alternative approach and more data when applied simultaneously under identical conditions to the same sample.

TRENDS

Ongoing expansion in the roles, applications and ranges of use of TA methods, together with continuing new equipment development, have all contributed to a rapid increase in their use in polymer science [2] and materials characterization [3], and a resurgence of applications in the earth sciences [4,5], particularly for fossil fuels [1,6,7]. Thus, for DTA/DSC alone, a list of some 26 areas of application has recently been published [1].

Clearly, over the last 25 years, TA has passed through phases of full recognition and consolidation to a period of rapid growth, brought about by simultaneous advances in six important directions. In this context, the references quoted herein have been selected to illustrate different aspects of "coal science thermal analysis", and to recognize the contributions of a wide range of authors. They cannot, however, be considered to represent a comprehensive coverage of the type recently compiled for DTA/DSC [7].

(1) The establishment by ICTA after careful selection, measurement and multi-laboratory evaluation of sets of fully certified reference materials, now available from the U.S. National Institute of Standards and Technology (NIST) as GM 758, GM 759, GM 760 and GM 761. Recently, simultaneous TA techniques have been applied to some of these materials [8].

(2) The increased refinement, use and application of the well established TA methods, i.e. DTA [9], TG [10] and DSC (to ~ 600 °C) [11].

(3) The development and increasing use of new methods, e.g. derivative thermogravimetry (DTG) [12], high temperature (to ~ 1500 °C) differential scanning calorimetry (DSC) [13] and its calibration [14], thermomechanical analysis (TMA) and DTMA [15], thermomagnetometry (TM) [16], evolved gas analysis (EGA) [17], emanation thermal analysis (ETA) [18], and thermosonimetry.

(4) The evolution of additional new techniques, e.g. "variable atmosphere thermal analysis" [1], whereby the furnace atmosphere conditions may be

pre-selected, maintained or changed as desired between [19] or during [10] TA runs, or pre-set combinations of different dynamic purge gases [20] or dynamic and isothermal [10] or quasi-isothermal heating conditions may be used [21].

(5) The coupling of TA techniques to give synchronous determinations of several parameters under identical conditions from the same sample, e.g. DTA/TG, DTA/EGA, DSC/MS, TM/EGA, DTG/ETA, DTA/TG/DTG, DTA/TG/MS, and TG/DTG/DTA/EGA.

(6) The invaluable series of overall reviews of TA established by C.B. Murphy and continued by W.W. Wendlandt [22].

Of these, the development and application of the concept of "variable atmosphere thermal analysis" is particularly important. This will be illustrated with pertinent examples. Its application to simultaneous TA determinations (e.g. DTA/TG) can be particularly valuable [23].

With this technique, individual reactions may be made to appear earlier or later, or be suppressed or enhanced [24], to produce greater sensitivity, give improved detection limits [25], and allow resolution of superimposed peaks [19], identification of minerals [24,26], determination of combustion characteristics [12,27], evaluation of organic content [28], analysis of coal proximate, ash or liquefaction residues, or determination of beneficiation [10,15]. Thus, different furnace atmospheres would be used for various coal determinations, as given below.

(1) Air or O_2 for combustion studies, including combustible and ash content determinations.

(2) Inert conditions of N_2, CO_2 or Ar for determinations of volatile yield, mechanical properties, mineral types, contents, and compositions;

(3) Different pre-set partial pressures of individual gases (e.g. CO_2) to effect some reactions preferentially, but not others, to promote identification and superimposed peak resolution;

(4) Nitrogen followed by O_2 or with traces of O_2 for proximate analysis or magnetic beneficiation, to remove pyrite/sulphur, respectively;

(5) Known contents of noxious gases such as SO_2 flowing over entrapment media, to evaluate their extraction value by weight gain under set conditions.

Coal TA studies in oxidizing gas conditions

On heating in air, coal burns to provide, on DTA curves, an initial small endothermic water loss peak; followed (between 250 ° C and a maximum of 900 ° C) by a very large rounded exothermic, typically doubly terminated feature, which is due to combustion of the volatile matter produced; followed by burning of the residual carbon [7]. These are called "combustion curves" [29], to distinguish them from the complementary DTG curves, "burning profiles" [12], while the corresponding DTG curves determined in nitrogen are called "volatile release profiles" [30].

Such determinations have been related to coal rank [31,27(1–3)], non-aromatic to aromatic contents [32], ignition temperatures [33] including charcoals [34], spontaneous combustion [35], calorific value [36,27(4)] and negative effects on this of minerals [37], the assessment of low organic content fossil fuels, washery reject material [28], and even combustion efficiency from residual fly ash carbon contents [31].

Coal TA studies in inert gas conditions

Under burning conditions, the smaller mineral effects on TA curves are swamped. However, in flowing inert gases burning is prohibited, and mineral effects show as clearly identifiable modifications of the now restrained coal/oil shale DTA [9] and TG [1] curves, whilst simultaneous DTA/TG determinations yield additional results [23].

Complementary to this finding was the discovery that when compared with N_2, CO_2 not only similarly prohibits coal burning, but markedly assists in carbonate mineral detection, identification, peak resolution [9] and separation from superposition on peaks of other minerals present [19].

Furthermore, of the carbonate decomposition oxides, only CaO rapidly recarbonates in an atmosphere of CO_2, to show clearly on DTA cooling curves as a sharp exothermic peak, thus detecting the "$CaCO_3$" component of calcite, dolomite or ankerite, free from interference by other superimposed peaks on the heating curve [24].

Additional studies comparing DSC results in N_2 and air have quantified the negative contributions to coal calorific values made by the carbonates magnesite, dolomite, ankerite and calcite. Siderite, by contrast, produces a small exothermic, owing to its decomposition–oxidation reactions [38]. The resultant application to calorific value upgrading after washing of high ash coals (taking into account the positive contribution of siderite) represents another new contribution by TA techniques [37].

Coal TA studies using different sequential gas conditions

The pioneering advance represented by the use of flowing N_2 followed by O_2 (N_2–O_2) to provide coal proximate analyses [39] has given reliable results within the limits of the standard method [35,40]. This has led to further TG applications, e.g. for pre-heated coal, bed, fly, and fluidized bed, ash (N_2–O_2–CO_2) and limestone (N_2–CO_2) [41] analysis of flue gas scrubber materials after use (flue gas–N_2) [42], comparison of sulphation, regenerative SO_2, and cyclic efficiency of sorbents (air–air + SO_2–N_2–N_2 + H_2–N_2–N_2 + air) [43], and analysis of solid waste refuse fuels (N_2–O_2) [44]. The TG modification TM has provided direct predictions of SO_2 yield from Fe (pyrite) contents in the absence of siderite (N_2–O_2–H_2) [45], and from the available Fe when siderite, Fe dolomite–ankerite are present with pyrite [46]. The technique may also be used for identification of members of the siderite–magnesite series [47].

With the development of high sensitivity specific gas non-dispersive IR detectors and small quadrupole mass spectrometers, EGA has become an important complementary technique, allowing the production of specific gas evolution profiles, alone or simultaneously with other TA determinations. This has led to further advances in detection limits for individual carbonates [48] and decomposition mechanisms–temperatures of individual minerals such as ankerite [49], or identification of different sources of sulphur present [17].

With the equipment currently available it is possible to perform simultaneously, using the same sample under identical conditions, TG, DTG, DTA (and DDTA if needed), or DSC together with determinations of several evolved gases such as H_2O, CO_2, CO and SO_2 or other gases such as O_2, SO and H_2, as required [50].

Such detailed coal utilization data on ash, formation temperature, composition and quantity have direct or potential applications to questions concerning formation, fusion temperature, fly ash composition [41], chemical stability, hydrogenation catalytic activity and residues [15], evolved gas pollutants (i.e. SO_x) and their extraction, entrapment–regeneration [43], and disposal.

CONCLUSIONS

Applications of TA to fossil fuel studies have expanded rapidly, and now range from burning profiles and low grade fuel value to mineral contents, compositions, decomposition characteristics and calorific effects; also proximate analysis, pyrite contents, detection of magnetic phases with application to coal beneficiation and EGA to flue gas extraction by sulphation and a range of sorbents (eg. limestone, dolomite, fly ash and calcium aluminates).

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