AN INTERPRETATION PROCEDURE

FOR

THERMOGRAVIMETRIC ANALYSIS

ON

SOUTH AFRICAN COALS

By

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Submitted for a PhD. Degree
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University of Pretoria
PRETORIA.
1988

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ACKNOWLEGEMENTS

The author is indebted to the following instances and persons:

1. The CSIR and Chief Director of the NICR for permission to use the research material for a thesis.

2. Professors C.P. Snyman and C.P.J van Vuuren for acting as promotor and co-promotor respectively, and their much appreciated guidance in the preparation of the manuscript.

3. Mr. M.C.J. van Vuuren, Assistant Director NICR, for selection and provision of the range of test samples.

4. Mr. J.M. Barnard and his staff for the petrographic analysis.

5. Mr. K.W.J. van Greuning and staff for the laboratory analyses.

6. Mrs. L. van der Merwe for doing the TG analysis and for the preparation of the illustrations.

7. Mr. R Malan for processing and styling of the document.

SUMMARY

Coal is a chemical compound with a complex composition. Proximate and ultimate analysis as well as physical and mechanical tests which are available do not furnish all the information required by industry.

Information regarding e.g. the burning properties of coal is required by furnace and boiler designers. Thermal analysis can be used for studying these properties using small masses of coal.

Differential thermal analysis (DTA) where temperature variations are measured which result from reactions which occur when coal is heated and thermogravimetric analysis, (TGA) where similarly mass variations are measured, are regarded as important.

Results from eg. TGA tests are usually interpreted without unified and formally accepted prescripts. It is desirable to investigate how the best use can be made of thermal analysis of coal, using DTA and TGA, and to devise a procedure for interpreting the results.

The problem is approached by studying DTA and TGA results obtained from a specially selected group of coals for which other analytic data are available. The samples were prepared according to the standard procedure for the laboratory analysis of coal.

At first, related information published by other researchers were integrated and parameters used by them identified and assessed in terms of fundamental scientific principles. Special experiments were conducted to probe the situation regarding orthodox kinetics of reactions and its related theory and observed discrepancies with regard to coal and its decomposition characteristics. It was found, along with other observers, that eg. activation energy values which are derived from TGA data should be used with extreme caution. In general an empirical approach for interpretation of results has much to offer.

A system is developed by which various thermal techniques, executable by a single instrumental arrangement can be identified by expressing them in matrix format using as indexes, heating arrangement, reactant type and reaction environment. S(1,1,2) e.g. designates a linearly heated mass of coal in air at atmospheric pressure.

To enhance the comparison of TG characteristics of similar coals they should be classified according to a matrix arrangement C(g,t,r) which is based on three index parameters namely, grade ie. the ash content, type ie. the vitrinite content and rank. A TG test provides the basic requirements for computing the indexes using formulae provided by the originators.

Information which can only be derived from a TG experiment e.g. S(1,1,2), are referred to as specification parameters. The information consists of e.g. a series of temperatures which identify specific reaction changes in the coal. Several other parameters can be derived. Coals are assessed by comparing their specification parameters.

Only two of the S(i,j,k) techniques are described in detail namely TG dispersion S(1,1,2) and drop furnace burnout S(3,1,2). The dispersion technique requires a linear increasing furnace temperature while the near sample temperature is also measured. This technique shows the decomposition stages of coal from dehydration to complete burnout.

The drop furnace technique, involves a sudden exposure of the coal to a hot furnace environment with free air access: Actual burnout of coal is emulated. The model is not perfect for combustion but the best that can conveniently be acquired for comparing the burning responses of coals.

To illustrate the type of information which can be obtained with other S(i,j,k) techniques experimental results of eg. a devolatilization test are presented.

Brief reference is made to the role that particle size plays during combustion and the importance of the composition of volatiles which are released is indicated by presenting relevant information from external sources.

The chemical composition and structure of the coals could not be determined but relevant information from an external source was presented which has a bearing on the practical analytic procedure which was described.

After a study of the group TG characteristics of the various coals and discussion of the conclusions which are justified a practical procedure is described according to which the equipment can be used both for routine or special purpose analysis of coal.

OPSOMMING

Steenkool het 'n ingewikkelde samestelling gevolglik voorsien die bestaande kort- en molekulêre-ontledings sowel as die fisiese en meganiese toetse nie altyd die inligting wat deur die industrie verlang word nie.

Inligting omtrent die verbrandingseienskappe van steenkool word deur die ontwerpers van oonde en stoomketels verlang. Termiese ontledings kan gebruik word om die verbrandingseienskappe van klein monsters steenkool te ondersoek.

Differensiële termiese ontledings (DTA), waar temperatuurverskille gemeet word veroorsaak deur chemiese reaksies in steenkool wat verhit word, en termogravimetriese ontledings (TGA), waar massaverlies deur verhitting veroorsaak gemeet word, is belangrike metodes wat gebruik kan word.

Aangesien resultate van bv. TGA normaalweg ontleed word sonder enige formele voorskrifte is dit wenslik om vas te stel hoe termiese ontleedmetodes soos DTA en TGA die beste benut kan word en om 'n prosedure waarvolgens gegewens geïnterpreteer kan word te ontwikkel.

Die probleem word benader deur DTA en TGA resultate wat van 'n spesiaal uitgesoekte bekende groep steenkoolmonsters verkry is te bestudeer. Die monsters is voorberei volgens standaard voorskrifte vir steenkoolontledings.

Aanvanklik is verwante gepubliseerde gegewens saamgestel en parameters wat gebruik word geïdentifiseer en beoordeel in die lig van toepaslike wetenskaplike beginsels. Spesiale toetse is uitgevoer om vas te stel bv. hoe betroubaar die kinetiese gegewens is wat van TG bepalings verkry word. Daar is gevind dat waardes vir aktiveringsenergie wat deur middel van TG vir steenkool bepaal word onbetroubaar is. Deur gebruik te maak van

empiriese metodes kan moontlik die beste grondslag vir gebruik van TG resultate gevind word. 'n Sisteem is ontwikkel waarmee bepaalde eksperimente wat deur 'n enkelsisteem van apparaat uitgevoer kan word in matrysformaat C(g,t,r) geïdentifiseer kan word. As indekse word gebruik, die aard van verhitting, soort reaksiemiddel en reaksie-omgewing. S(1,1,2) bv. dui aan dat 'n liniêr stygende oondtemperatuur gebruik word om steenkool in lug te verhit.

Vir beter ontleding van die TG eienskappe van soortgelyke steenkole is dit wenslik om 'n vorm van klassifikasie toe te pas. 'n Matrys met indekse wat bepaal word deur kwaliteit dws., as inhoud, tipe dws. vitrinietinhoud en rang. Die indekse word bereken van TG gegewens deur gebruik van formules wat deur die ontwerpers van die stelsel voorsien word.

Gegewens wat slegs van 'n TG toets verkry kan word, bv. S(1,1,2), word spesifikasieparameters genoem. Die inligting kan bv. betekenisvolle temperature wees wat bepaalde reaksies aandui. Verskeie ander inligting kan verkry word. Die spesifikasie parameters word gebruik om steenkole te vergelyk.

Van die reeks S(i,j,k) tegnieke word slegs twee in besonderhede beskryf nl. TG dispersie S(1,1,2) en die valoond S(3,1,2) tegnieke. Vir TG dispersie word die steenkoolmonster verhit teen 'n liniêr stygende temperatuur terwyl die temperatuur naby die monster ook gemeet word. Hierdie tegniek dui aan hoe die steenkool opbreek in verskillende chemiese komponente vanaf kamertemperatuur tot volledige ontbranding.

Die valoond behels nabootsing van werklike volledige verbranding. Die steenkool word skielik blootgestel aan 'n hoë temperatuur in 'n oond met vrye lug toegang. Alhoewel die model nie ideaal is nie dien dit die doel om die brandbaarheid van verskillende steenkole te toets.

Ten einde 'n aanduiding te gee van die aard van resultate wat met enkele ander S(i,j.k) tegnieke verkry is word 'n voorbeeld van 'n ontvlugtingstoets verstrek.

Die belangrike rol wat korrelgrootte in verbranding speel word vermeld asook die samestelling en rol van vlugstowwe waarvoor toeligting uit gepubliseerde bronne verstrek word.

Die chemiese strukturele samestelling van steenkool is van groot belang. Alhoewel, vanweë instrumentele probleme kon oorspronklike inligting egter nie verstrek word nie. Baie bruikbare gegewens kon egter uit gepubliseerde bronne verkry word wat tot groot waarde was om die TG onledingsprosedure te ontplooi.

Na bestudering van die groepeienskappe van die TG resultate van die toetsmonsters is alle betekenisvolle gegewens benut om die resultate van TG tegnieke te interpreteer.

1 INTRODUCTION

Several methods exist for determining the properties of coal. The methods include chemical analysis, petrography and various mechanical test procedures. Results of these analytical techniques are used in a general sense to ensure conformity of coals to a given standard, or to select the best type for a given industrial use.

One of the objectives of this study is to consider the use of an additional method of coal analysis which involves weighing the coal sample while heat is applied to it. This system, referred to as Thermogravimetric Analysis (TGA), holds the promise to reveal further useful information eg about the heat yielding properties of the coal, which cannot be deduced from the standard calorific value determination.

A very elementary illustration of how the mass of a coal sample varies when it is heated at a linear rate is shown by Figure 1.1

The background against which the TG system for coal analysis is to be assessed requires explanation before the system and its attributes are described.

All standard methods of coal analysis have been developed to a high degree of sophistication and are in common use. However, as a result of continuous industrial development specific detailed information which is required is not adequately furnished by the standard techniques. Definition of these requirements, as well as the provision of equipment for their measurement, and a description of procedures for their application and interpretation are necessary.

Demands for diagnostic data derive from all three major sectors where coal is used, namely combustion, production of chemicals, and carbonisation. Although TGA can be used to advantage in all three these fields of utilization, only its applications relating to the burning of coal will be considered.

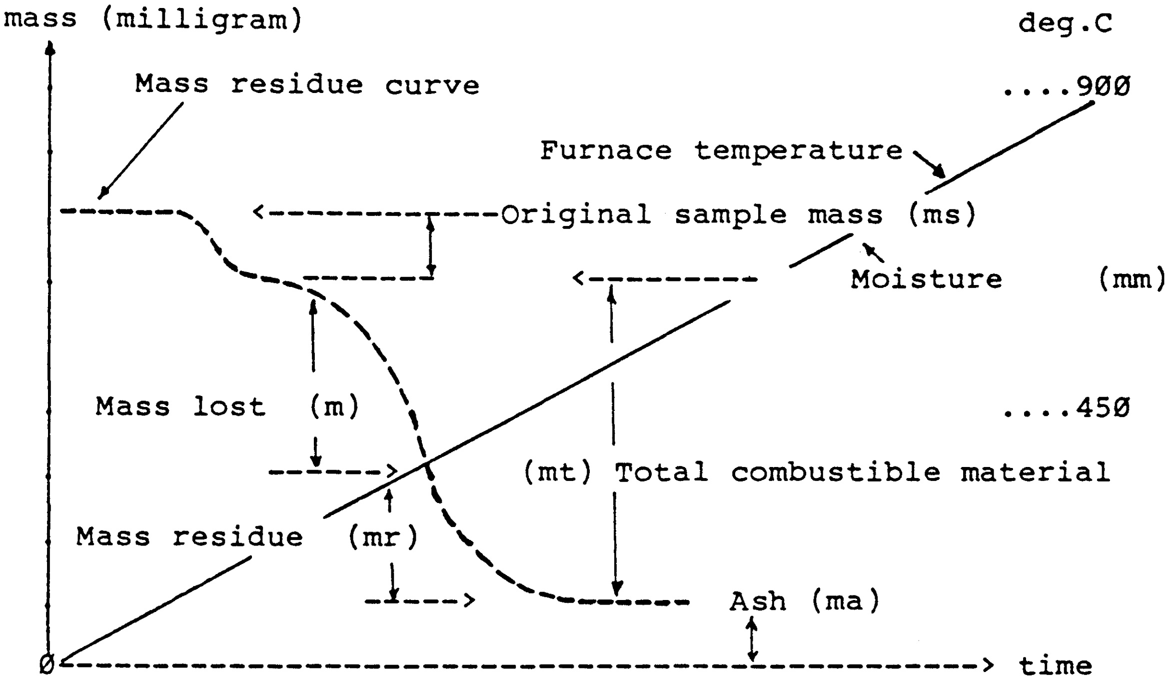


FIGURE 1.1 The Mass Residue (MR), and furnace temperature (Tf), curves

(Symbols refer to mass)

The chemical analysis values which are commonly determined on coal are the percentages of moisture (MO), ash (AS), volatile matter (VM) and fixed carbon (FC). These are referred to as the proximate analysis. A further group of chemical data involves the elemental constituents of the coal viz. the percentages of total carbon (C), hydrogen (H), nitrogen (N), sulphur (S) and oxygen (O). This is referred to as the ultimate analysis. (In general and where appropriate symbols will be typed in capitals when referring to laboratory results and in small letters when referring to TG derived data.)

The potential heat which a coal can release, ie the calorific value (CV), in MJ/kg, is also determined under standard conditions. The heat of combustion is determined by oxidizing very fine coal in a steel container in the presence of oxygen and water vapour at an initial pressure of about 25 atmospheres (Findlay, 1943, p 303). The pressure could be doubled during the exothermic reaction which means that efficient oxidation, and eventually, complete oxidation is ensured.

In commercial furnaces, where coal is being burned for the generation of heat, pure oxygen under pressure is hardly, if ever used, and burning generally takes place in air at atmospheric pressure.

A point to note is that the calorific value can be computed as if the experiment had proceeded under atmospheric conditions, but whether identical reaction sequences would be encountered in free air and in the calorimeter bomb, is rarely, if at all, commented on. It may be possible that in the bomb, exothermic processes could occur which are not possible under atmospheric conditions; additional information about what happens in the latter case is therefore necessary. In this regard Sarkari, (1982, p 676) can be quoted: "In a boiler, mixing of air-fuel is inadequate, and the temperature conditions are poor compared to those in a bomb calorimeter. There is always some unburnt carbon left over, no matter how good the furnace is, and the quantum of inherent unburnt coal has a direct bearing on the ash quantum". Different approaches, towards direct assessment of the heat producing potential of a coal requires consideration, eg the concept of thermal flux, as explained by Bosworth (1956, p 75), may provide a practical means through TG applications. Differential scanning calorimetry (DSC) techniques are based on these principles and can eventually be incorporated.

Boiler designers are constantly attempting to construct furnaces which will lead to better combustion and for this purpose information that relates to the actual burning behaviour of the coal to be used is required, eg the rate at which the coal burns, how the volatiles are released and what grain sizes would produce the most stable flame. Generally these properties cannot be measured directly and various ways of inference must be devised.

To assist in attaining maximum heat from coal, all possible information should be acquired which can assist in determining the quality of coal which will perform best under certain conditions.

Petrography involves the use of the microscope to determine the physically distinguishable organic entities (or macerals) of the coal as well as the mineral matter that it contains. It should be advantageous if a means could be found by which the role that these maceral groups play in burning, could be established and made available for use, amongst others, in the design of furnaces.

For the large scale evaluation of the practical heat generating performance of coals, test boilers are used which are heated by different standard burners such as, eg chain grate stokers. The coal is evaluated in terms of the quantity of steam that one mass unit of coal can deliver at a given temperature and pressure. The test is expensive, requires a large quantity of coal and takes several hours to complete. It is therefore costly and cumbersome to study, the effects of eg different grain sizes of coal by repeated trials, using this equipment. Large quantities of coal for tests are not always available and techniques which can produce information relataed to this, using smaller quantities of material, even if less precise, are desirable.

Several similar bench- and pilot plant-scale installations are available for testing the burning properties of coal used in pulverized fuel (PF) furnaces. One of these is described briefly: It consists of a heated tube through which a stream of air loaded with fine (ie 0.05 mm diameter) coal particles, is blown at different velocities and with different coal loads. Amongst others, the amount of unburnt carbon is determined in the material recovered at the exit of the tube furnace. This "drop tube furnace" equipment is also expensive, but relatively small quantities of coal are required for testing. The operation time, together with the determination of the unburnt carbon etc. involves considerable time. In this respect faster operational and small sample techniques can be useful.

It is therefore clear that in general some vital information concerning the burning properties of coal is lacking and that it cannot be derived from any of the parameters that are normally determined. Two predominant areas of investigation are broadly indicated namely, the mechanism of the heat producing processes and the effects of the physical nature of any particular coal on its burning history eg coal burn out times determine how long different particles must stay in the combustion chamber to release all their heat. A way must be found to derive this kind of data and to express it in unambiguous quantitative terms. In this regard computer simulation becomes eminent because some information cannot be determined by experiment and reasonable estimates must sometimes be used as the best approximation to the solution of such problems.

The simulation technique first involves a study of the general behavioural trends of eg granularity or ash on burning. These trends are then formulated mathematically and entered into a programme by which they can be studied while the process is simulated on a computer under controlled conditions. Interpolations or extrapolations can then be made for hypothetical model outlays which represent practical situations. The reaction rates for burning processes are of importance in this regard.

In order to meet the stringent demands for this kind of analysis the relations between the laws of chemistry and those which govern TG data need to be established as accurately as possible, but without undue elaboration. In this regard no unambiguous chemical basis for the combustion reactions of carbon or coal could be established from the literature. Furthermore, no fundamental and authorative guidance on the principles which must be applied appears to be readily available. It is therefore difficult to approach research on the thermal response of coal on a basis of unquestionably established scientific principles. This is corroborated by the following statements concerning the interpretation of TG data:

1. Wagoner et al, (1967, p 6) claims that for their version of the method : "The burning profile test as developed is an empirical one".

2. Daniels (1972, p 60) comments as follows: "In general therefore, there is no universally accepted or universally applicable method of computing TG curves and each worker is left to evolve a procedure suited to his own system."

3. Blazek (1973, p 71) comments on the usually accepted rate equation used for computation of kinetic parameters,

$$da/dt = k(1-a)^n \qquad \text{E1.1}$$

where,

a = fraction of the sample decomposed
k = rate constant
n = reaction order
t = time of the reaction as follows: "However it is unlikely that the dynamic technique will ever find universal application because the rate expression is not applicable to all solid-state decompositions". This is in agreement with the view expressed by Daniels (1972, p 62).

4. Serageldin et al (1983, p 12) assumed the rate equation to be valid for TGA and three different calculations based on it, gave results for the activation energy of the same coal, to vary within ranges (a) 25 to 70 kJ/mole, (b) 400 kJ/mole and, (c) 100 to 200 kJ/mole. Any analytical basis which accommodates such a wide range of values for a supposed constant obviously suffers from severe limitations, one of which is that it is virtually impossible to define a mole of coal.

The implications of the complexity of a solid state reaction must also be pursued in relation to the size of the burning granule. Regarding experimental data on larger sized coal and carbon particles (diameters > 0.15mm), Essenhigh (1970, p 7) comments, "This implies that the reaction was totally dominated by the boundary layer diffusion and was also first order with respect to the ambient oxygen concentration". However, he later concludes, (p 8): "....the balance of probability from this evidence only lies in favour of a zero order reaction, with high activation energy, implying desorption dominance."

The fact that these authorities are cautious about the interpretation of experimental data leaves scope for consideration of additional information which may assist to cast light on the complex problem of the burning of coal. The following symbolic representation for the reaction when a piece of coal is heated may serve to elucidate the problem. In this equation the prime variables are q, coal and air:

$$q + \text{coal} + \text{air} \text{ --- } \text{C-vol} + \text{X-vol} + \text{R-vol} + \text{ash} + Q \qquad \text{R1.1}$$

where:

q = The heat required to break down the coal into components which either react with the heated air or are released into the atmosphere.

C-vol = Volatile products derived from or associated with carbon in the coal, ie "organic" volatiles.

X-vol = Volatile products derived from mineral matter in the coal.

R-vol = Volatiles derived from reaction between volatiles and/or solids in the coal and oxygen in the air.

ash = Inorganic residue resulting from the impurities in the coal.

Q = Heat released either by changes of state ie latent heat or by various exothermic reactions.

A homogeneous reaction between pure substances, and a heterogeneous reaction like R1.1 are similar in that no reaction will occur until q has reached a specific value. In the case of coal it depends on the composition of the coal. A definite minimum temperature must also be maintained to sustain the reaction. Depending on the value of q at various temperatures, several reactions could be observed during R1.1 but the true nature of these phenomena may be obscure, eg CO_2, may be liberated but it does not have to be a reaction product of the carbon in the coal. One of the problems of coal reactions is to determine the real cause of an observed phenomenon.

In the symbolic representation of R1.1 the word coal, reveals nothing to characterize it in terms of invariant chemical components, and therefore no quantitative deductions or predictions can be made from the reaction. It is therefore imperative to characterize a coal in terms of its proximate, ultimate and petrographic parameters before it becomes a known variable in the symbolic expression of the reaction.

Coal, in contrast with eg NaCl, has no fixed atomic structure but when characterized by its ultimate analysis, a stoichiometric computation can be made of the total expected heat of formation during burning according to the following hypothetical reaction:
$q + C_vH_wN_xS_yO_z + \text{oxygen} \text{ -->} pCO_2 + rH_2O + sNO_2 + uSO_2 + Q$ R1.2
where v,w,x,y and z represent the percentages of the respective elements. Note that no information is given regarding the reactions which actually occur.

For bulk reaction responses the principles of chemistry do apply but the reactions cannot always be individually identified. Quite often the resultant response must therefore be interpreted, sometimes using unorthodox methods. To some extent this can be attained by means of TGA which measures group effects, which may be characteristic of a particular coal.

The maceral composition of coal can in principle be determined quantitatively although the identification of some macerals is rather subjective, but it is sufficiently diagnostic when an attempt is made to explain unknown features of TG results.

All these coal parameters will be used to establish the usefulness of TG applications in determining the burning characteristics of coal. Against this background the purpose of the research is to develop an analytical procedure based on the application of heat to coal in various ways, and to use the results to predict the performance of a particular coal as a fuel in comparison to others.

A group of coal samples of varying grade, type and rank was specially selected for this purpose. The results however only indicate special features of TG analysis of coal and do not reflect similar properties of all SA coals.

2 BASIC PRINCIPLES AND TECHNIQUES OF THERMAL ANALYSIS

Of the total range of thermal analyses which are possible, only DTA and TGA will be considered for present purposes. DTA involves the study of the heat absorbed or liberated during reactions by measuring the temperature changes of a reacting substance relative to an inert substance, within a given thermal environment. TGA, involves the measurement of the mass changes of a substance during heating.

In the early stages of development of these methods the measurements were made on an analogue basis, ie the results were plotted continuously for the experiment. If other data operations were required, eg differentiation, special electronic circuits were needed in the recording unit to perform them. These results were then again produced as a graph. If readings were required they had to be scaled by hand from the graphs. A description of various TG systems and the principles of analysing data on the basis of the graph features are provided by Brown (1982): The interpretation of results from coal is not discussed.

Later on use was made of the advantages of digitized equipment, both in terms of experimental control and data reduction. The fast responses that can be obtained with microcontrollers made it relatively easy to combine different methods into a single experimental setting, and it is quite possible to combine TGA and DTA in a single experiment. The temperature and mass recordings are made under control of a single computer module and the results stored in various ways as time synchronized data strings.

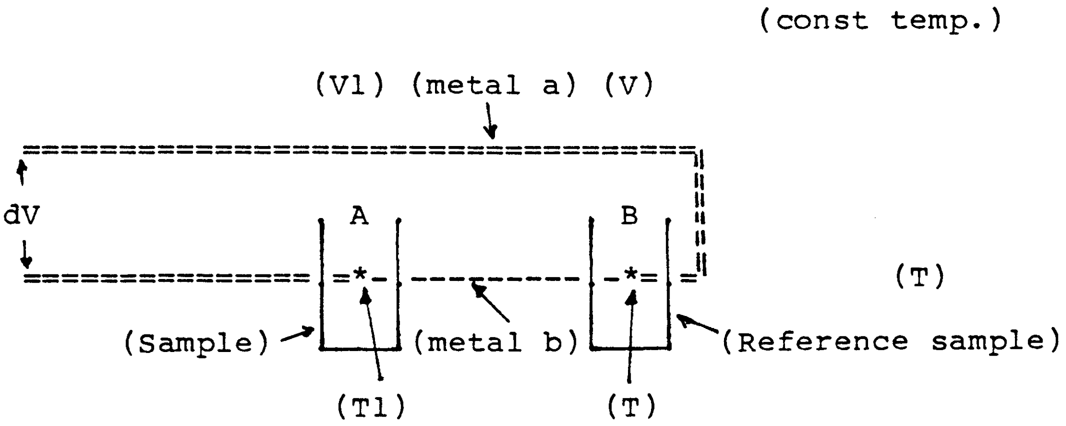
This information is then processed by computers using standard ways of presenting the results; the experiment can also be completely independent from the manner in which the data are processed.

2.1 Differential thermal analysis (DTA)

A typical schematic layout for a DTA system is shown by Figure 2.0

DTA involves measurement of the temperature differential between an inert reference sample B, and a sample A in which an endothermic or exothermic reaction takes place within the same external thermal field. Differential thermocouples are used to measure dT with reference to T. The dT values are plotted against the ambient temperature. Deviations above the ambient temperature indicates exothermic and deviations below, endothermic processes. The normal instrumental layout is for convenience and individual measurement of T1 and T by other methods can also produce dT, or a value which is proportional to it.

Dobal et al (1982) studied the DTA response of coals and found that the oxidation degradation of the samples occur in five regions. He also made an important remark about the results: "So far we have not been able to decide whether the properties of such systems are given by properties of individual components, or the system as a whole forms new properties which cannot be derived from the behaviour of its components." It is stated in conclusion: "The DTA method in an oxidative atmosphere together with Py-GC allows a study of the material structures with respect to their past. Some very different structures on the other hand may give similar results and for these reasons our interpretation may have to be careful." (Py-GC: Pyrolysis Gas Chromatography). Warne (1982) directed attention to the minerals which occur in coal and the identification of their specific responses. The following remarks are significant: "The DTA curves of coal and oil shale determined in air show a large, rather ill defined exothermic feature, which varies somewhat in temperature (dependent on the type of material), within the temperature range 250 to 900°C".



$dV = V1 - V$

$dV = k1.(T1 - T) = k1.dT$

V1 & V are thermo-couple voltages.

T1 is the temperature of the sample.

T is the ambient temperature.

FIGURE 2.0 A differential thermal analysis system

Warne studied the DTA responses of minerals which are commonly found in coal. These include calcite, magnesite, dolomite, ankerite, siderite, kaolinite, montmorillonite, illite and quartz.

It was found that the small responses of the minerals in coal are masked by the extensive exothermic carbon reaction. Sometimes the reaction temperatures for different minerals overlap, or the effects may be of an opposing nature. The use of an inert gas, or pure oxygen, as reaction environments may enhance the DTA effects and combining DTA and TG could improve matters so that positive results can be attained.

2.2 <u>Thermogravimetric Analysis (TGA)</u>

Application of TGA must date back many years, since today it has well established uses in several scientific fields for which commercial instruments are optimised. Essenhigh and Howard (1966), state that studies on combustion were conducted as early as 1667. With commercial instruments analyses cannot always be properly done on account of the small sample size and special designs are necessary to meet specific requirements.

Thermogravimetric analysis is applied widely in pure chemistry, biology, medicine, materials etc. as is shown by the contents of The Proceedings of the Eighth International Conference on Thermal Analysis ICTA 1985, Vols 1 and 2. Only 18 of a total of 380 papers deal with burning of wood, coal or graphitic products which show that coal is not a prominent material for thermal analysis.

Instruments for analytical purposes are consequently designed for the fields in which the greatest demand exists. Attempts are therefore made to deal with extremely small quantities (10 to 50mg) of material and containers are small and sometimes deep. These features are not suitable for analysing coal, particularly when the experiment is carried out in the presence of pure oxygen. In this respect the comment of Dobal <u>et</u> <u>al</u> (1982, p 1254) concerning the analysis of a multicomponent heterogeneous system (MCHS) for thermal analysis should be noted: "More significant for the characterization of MCHS appear to be methods that work with the sample as with the whole(*). Furthermore, the most reliable procedures in evaluating the behaviour of these systems in technological processes are still those that imitate the process itself." (*)"Whole" probably signifies the expression "thing complete in itself" ie the coal as it is.

3 SPECIALISED TGA OF COAL

Thermogravimetric analysis of coal covers a wide range of applications and can be optimised in various ways:

Determination of the moisture, ash, volatile matter, and fixed carbon contents received attention from various investigators associated with instrument design eg Earnest (1985), Baur (1983) and Elder (1981). Other scientists in the fields of furnace design and basic research also made contributions. These include Cumming and McLaughlin (1982) and Saayman (1985). In general, it appears that for purposes of bulk analysis of coal, it will be difficult to improve on the accuracy of the standard laboratory methods of proximate analysis. An advantage of TG techniques appears to be that these parameters can be obtained as a bonus, and for this reason a slightly lower standard of accuracy can be tolerated for this "quasi-proximate" analysis, especially when the data are used for the broad categorization of coals where constraints are not very stringent.

The calorific value is normally only determined by the standard bomb-method but other empirical approaches are possible; it can be computed from the volatile matter and carbon content or the ultimate analysis of the coal.

Attention was also paid to some of the deleterious constituents in coal such as sulphur. Almer et al (1982) based his determination of sulphur on the magnetic properties of pyrite whereas Frazier et al (1982) made use of the transformation of sulphides to calcium sulphate. This involves the capturing of sulphur within a furnace, by means of lime at high temperature so that it will not be released into the air as sulphur dioxide or sulphur trioxide.

Burning properties of coal were also considered by investigators such as Wagoner and Duzy (1967); Borio, Goetz, Lao, Metha and Nsakala (1982); Cumming and McLaughlin (1982) and Juntgen _et al_ (1987). It was realized that an important aspect of TG applications was the specific information which could be obtained about the burning behaviour of coal. Wagoner and Duzy compared TGA curves of standard coals which performed satisfactorily in furnaces of a particular design with those from unknown coals by inspection.

Certain variations in form could be interpreted in terms of specific furnace designs that would ensure efficient burning of the coal. Borio integrated a group of tests, using different instruments, on burning coals to establish how furnaces should be designed for most efficient combustion of the coals. Juntgen studied a range of coal properties, varying from ignition of fine particles to the release of volatiles, in order to establish how coal responds when it is heated in different ways.

Aspects of combustion kinetics were investigated by Serageldin and Ping Pan (1983); Zeldowich, Barenblatt, Librovich and Makhviladze (1985), Juntgen and Van Heek (1979) and Cumming (1984). These observers studied the application of the rate constant and Arrhenius equation to the data obtained from solid state reactions using TG and other observational techniques.

A practical approach towards understanding combustion under commercial conditions and the associated problems was presented by Sarkari (1982 - 83). This series of publications is instructive for directing research towards problem areas.

Finally the theory of and mathematical approaches to combustion were handled amongst others by Essenhigh _et al_ (1966) and Buckmaster _et al_ (1982). The work of these authorities, which is of a basic scientific nature, gives an insight into various analytical approaches and the subtle distinction between burning and combustion.

3.1 Previous work

TG applications of present interest to coal are quoted by Van Krevelen et al (1957, p 317), referring to work of Oreshko (1949). It is not known who first investigated coal by means of TGA, but the publication which had a profound effect on the present research was that by Wagoner et al (1967), in which the application of TGA for the determination of burning profiles was given. These authors (op cit, p 2) indicated that "The objective of this study was the examination of oxidation rates of fuels from ignition to completion of burning". In a later publication, in which interpretation procedures related to the boiler industry were described, it was stated that "The profile is a characteristic fingerprint of the fuel oxidized under standard conditions, and is not intended to provide absolute kinetic and thermodynamic data" (Wagoner et al 1973, p 119). An ad hoc application, ie solely for the design of furnaces, was envisaged.

In most of the earlier publications determination of the proximate parameters was presented as a major achievement. Various schemes were devised to obtain results which are comparable to those achieved by standard procedures. The switching of heating rates and of the ambient atmosphere from nitrogen to oxygen, attained improved proximate values but these procedures complicated the extraction of other information from the TGA data.

With additional experience it was realized that the most significant contribution of TGA to coal research lies in the information it can reveal about the manner in which coal responds to heat as well as the detail it can furnish to supplement proximate analysis data. Dobal (1982, p 1254) expresses this aspect very clearly: "MCHS (multicomponent heterogeneous systems) have one characteristic peculiarity, which is their history. In their structures they have coded paths along which they were getting to the form we observe." It should be noted that this property can best be documented from the behaviour of a coal sample in the pan of the mass balance during heating. When the reaction products are analysed, a different picture generally emerges. When considered in analogy with a real furnace TGA represents a study of the coal as observed from the feeding end, while the other alternative is to study the composition of the effluents. To distinguish, and for good analytical reasons, the first approach is referred to as burning studies and the latter can more appropriately be described as combustion studies.

Combustion studies were amongst others carried out by Gomez and Vastola (1984). The technique was summarized as follows: "A quantitative differential technique for studying the coal particle combustion process and particularly the ignition step was developed. The approach is based on the continuous and simultaneous analysis of the carbon monoxide and carbon dioxide produced when a captive single coal particle is burnt after injection into an isothermal flow reactor swept with a preheated oxygen nitrogen mixture". This shows that different analytical procedures are required to understand the overall response of coal to heat.

As progress was made with purely chemical approaches it was realized that coal had other properties (eg its maceral composition) which could be correlated with its thermal response characteristics. More precise identification of the properties of coal is thus indicated. The foundations for such an integrated system, considered from the petrographic end were furnished, amongst others, by Snyman (1976) and Hough et al (1985). Other investigators studied the influence of coal rank on combustion, eg Field (1970) established that the reaction rates of coals can be expressed in terms of a diffusional and a surface reaction rate coefficient. A quantitative means of expressing response characteristics is thereby introduced which most likely refers to volatile and char response components.

At the NICR these concepts were well noted and research was directed and equipment developed in an attempt to test, and if possible to extend, the outlined principles described by Wagoner and associates.

3.2 The TG System for coal analysis at the NICR

To maximize the range of usefulness of the equipment to the coal industry and to facilitate data handling, the final form of the equipment and interpretation procedures vary considerably from the model presented by Wagoner and Duzy (1967, p 3). Both observation and reduction operations are computer based so that results are available in a format suitable for anticipated future demands by the entire industry, ie it can form an integral part of an interlinked data base system for coal.

Figure 3.1 and later Figure 3.1b, (p 66) show schematic layout of the experimental and reduction settings for systems that are dedicated to studies of the manner in which the coal decomposes, the first is referred to as **TG Dispersion Analysis.**

A 300 mg, -70 mesh, coal sample unacclimatized for moisture, is suspended from a mass balance to hang in a furnace which slides upward to accommodate the solid platinum container which holds the sample. Two thermocouple elements are placed in the furnace. T2 is very close to the surface of the coal sample while T1 is about ten mm below the sample pan. T1 senses the ambient furnace temperature and is recorded by the control computer A2 (Intel 230) and used to maintain the furnace at a linearly increasing temperature through processor A1, (Intel SBC 80/10A) which executes the various types of programme. T2 registers the approximate sample temperature which is stored in the memory of A2, along with the recorded mass value at selected sampling intervals, for the duration of the experiment.

Air is passed into the furnace from the bottom at a rate of 35cc/s. It passes through glass wool to spread it for gentle upward migration through the furnace, by-passing the pan and eddying above it, to ensure an overall even, overhead only, air supply. The coal is very slightly starved of oxygen so that decomposition is enhanced before ignition sets in

Processor A2 monitors the experimental progress and provides various displays which can be used for control changes where necessary.

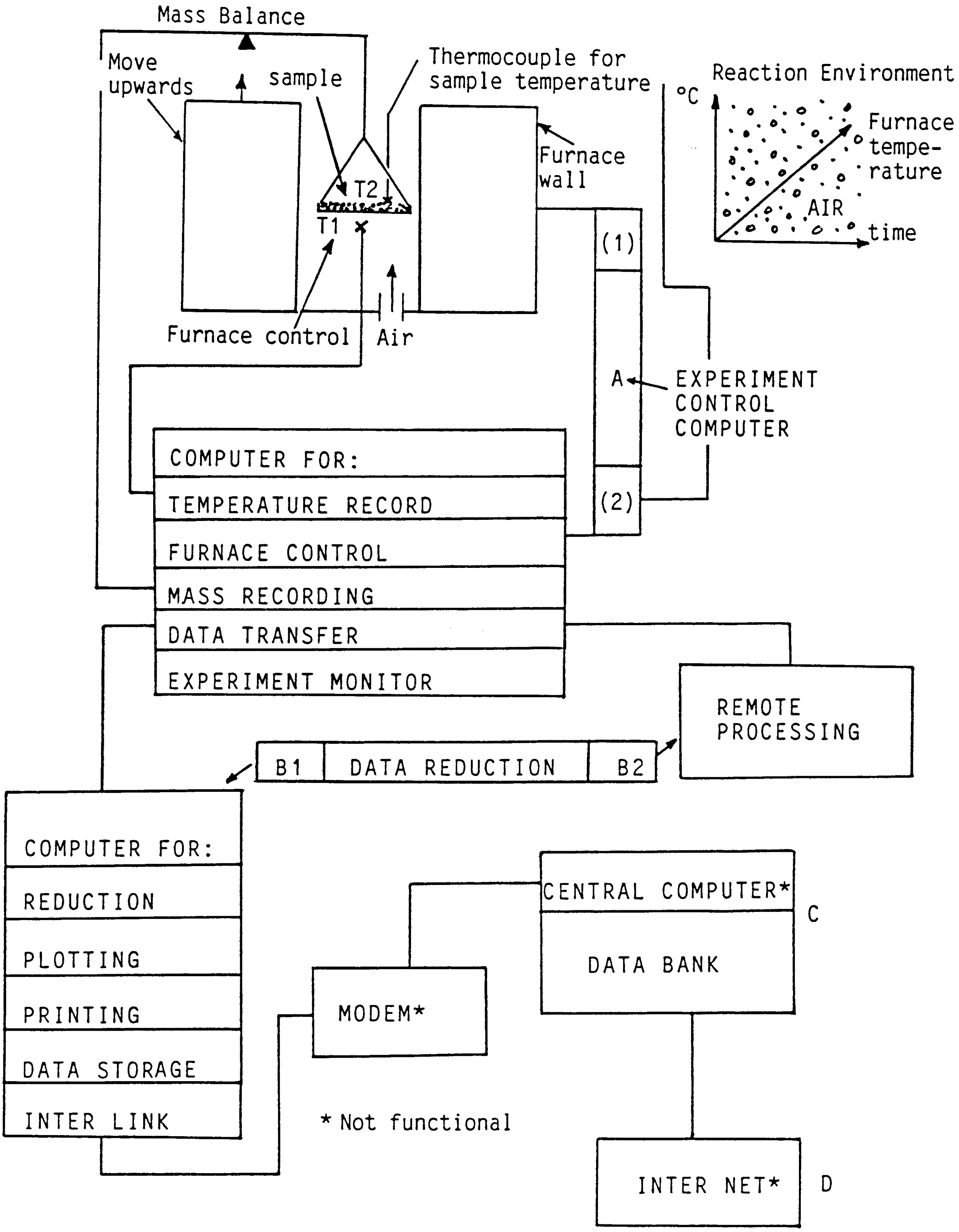


FIGURE 3.1 TG Dispersion experimental arrangement

After completion of the experiment the data are transferred through a standard RS-232 serial transmitter, which can also be used for remote control purposes, to the reduction computer systems B1 (CBM 3032) or B2 (CBM 720) which can be short or long distances away from the experimental set-up. This modular outlay of the equipment has definite advantages concerning both research and commercial applications of the TG method:

1. The sensor can be constructed as a robust unit for remote usage.
2. Any standard computer can be used for reduction purposes.
3. Programs can be developed in standard high level languages for individual requirements.
4. Semi-real time data utilization is possible.
5. Operational skill requirements are reduced to a minimum.
6. Multi purpose techniques can be effected using a common sensor unit.

At the NICR the objective set for design was to use one basic recording and control computer which is flexible enough to operate on a variety of sensors, and to cover as much of the experimental data as possible. The sensors, ie essentially different types of furnaces and mass balances, were optimised to produce the most desirable data which relate to the TG analysis of coal. As much data recordings as possible are made, and stored on diskette. Various reduction programs were developed to produce different kinds of results. Establishment of sound scientific principles on which these reductions can be based is an important directive for the research that is done.

For selection of a range of options for specific TG experiments that can be done and for which TG data will be comparable, the general background of the total possible range of choices requires consideration. This can be done most conveniently by arranging the prime variables in matrix format. This will enable easy reference to the total scope of the analytic variations which are possible. Results from some of these procedures which are applicable to coal, and which can be executed with the equipment at hand, will be provided.

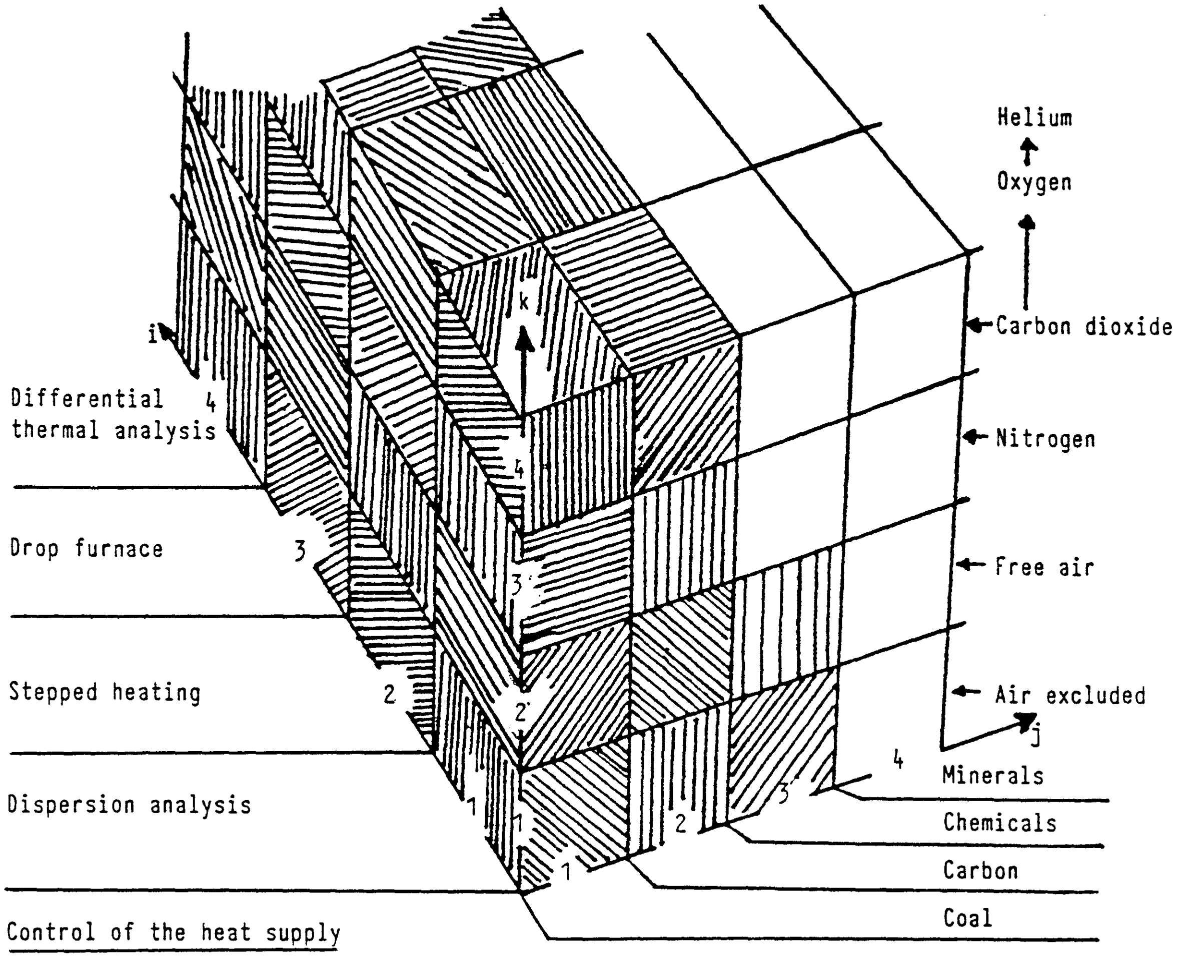
If the prime variables of a particular TG experiment, which are all completely independent namely: 1. thermal activation, 2. reactant characteristics and, 3. the reaction environment are considered as the i, j, k indexes of a presumed **TG Experiment Specification Matrix,** S(i,j,k), (R1.1), the row, column, and stack indexes will respectively show up as shown by Figure 3.2. These variables are shown as functional operators on the left side of R1.1 (page 6).

Figure 3.2 shows that, eg S(1,1,1), will represent a TG experiment where the sample is heated at a linear rate ie the i row with index 1; coal is processed, identified by the j column with index 1; the environment will be free of air, indicated by the k stack with index 1.

Each indexed prism of the matrix block thus represents a unique experimental setting for which the results can be compared with other settings and or reactants. The specific combinations which are investigated are shown by cross hatching of the matrix reference blocks. In this manner the extremely wide range of different TG experiments can be visualized easily, and defined with precision, using different index combinations of the S() matrix. Specific names are also given to the most popular techniques.

The matrix element, S(1,j,k) refers to the TG dispersion technique including all its ramifications. S(3,j,k) similarly indicates instantaneous heating (ie the drop furnace technique). Within the defined range it can be seen from Figure 3.2 that 36 different layouts are envisaged for use in connection with the analysis of coal and coal analogues, but more are possible. All the techniques require the same hardware but different software control and reduction algorithms.

Apart from all these variations, the equipment, by proper scheduling, can be used to determine the proximate analysis, ie mo, as, and vm.



i = heating conditions ; j = type of reactant ; k = reaction environment

FIGURE 3.2 The experimental state matrix S(i,j,k) for the variables of thermal and thermogravimetric analysis

3.3 The TG dispersion technique

The fundamental technique, S(1,1,2), was originally developed by Wagoner et al (1967 & 1973), and referred to by them as, **"The TG Burning (Combustion) Profile"**. However the technique is now referred to as **TG Dispersion Analysis,** because a range of reaction processes, not only burning, are imposed on the coal sample.

The dispersion technique represents a variation of the "Burning Profile" of Wagoner et al (1967). The modifications include the introduction of a system to measure the approximate temperature of the sample in conjunction with that of the furnace. This temperature assists in the identification of certain critical stages during the heating of the sample at a constant rate of 17°C/min. The mass of oxygen per unit volume in the furnace, is reduced due to expansion of the air from room temperature to 1000°C. The sample is large enough to cause a local "hot spot" in the furnace, after ignition has occurred. The heat which is released is relatively intense but the burning response is recorded only by the nearby thermocouple.

The thermal effects of other possible reactions eg decomposition of clay minerals and subsequent crystallization of the reaction products, are too small to effect the particular recording, and furnace control, arrangements.

3.3.1 Physical characteristics of the mass loss (ML) curve and its interpretation

The mass loss (ML) curve expresses the cumulative mass that is lost as volatile components which are liberated as a result of breaking up of the molecular structure of the coal or products of reaction which are formed through reactions with oxygen from the surrounding air. The ML curve simply expresses the difference between values of the mass residue (MR) curve, as in Figure 1.1, and the start mass of the sample.

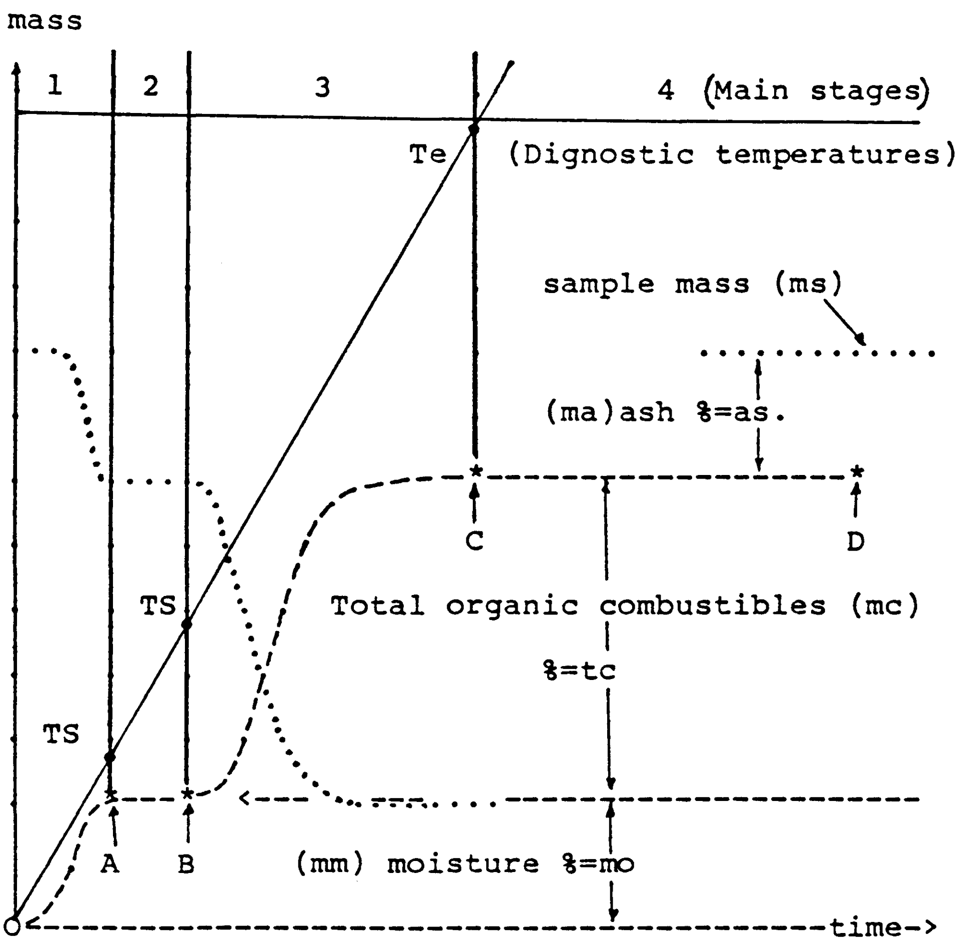
Figure 3.3 shows two idealized cases, where no change in mass occurs, ie the two lines (terraces) marked AB and CD. From the mass fractions (ma), (mc) and (mm), the percentage values for ash, as, total combustibles tc, and moisture, mo, can be derived. By marking, (*) the end points of the time stretches over which the mass remains constant (these could be of much shorter duration than eg AB), the dispersion process can be subdivided into stages of development (conversion), which represent various main reactions which occurred (shown by the vertical lines which mark the stages).

The transitions between stable states, (steps) are represented by the transient forms, ie the flexures of the ML curve such as eg BC. The mathematical features of these curves, (segments) reflect information about the processes which are involved. When transitions are fast the steps are almost vertical but for slower processes they become sigmoidal. The procedure for systematic analysis of these features forms the basis of a quantitative analysis of TG data.

The elementary principles demonstrated for Figure 3.3 will be extended using observed data. To explain the diagnostic features of a TG dispersion mass loss curve various cases representing different degrees of complexity will be analysed in a similar fashion as on Figure 3.3 with elaborations where necessary. It should be noted that the following series of illustrations represent cases where the main stages shown by Figure 3.3 become extended and/or subdivided, as a result of specific diagnostics which cause the formation of second and third order subdivisions and ending with a final compartmentation which is called phases.

3.3.1.1 TG analysis by identification of stable states

Figure 3.4 shows the mass loss curve, obtained in a TG dispersion analysis, S(1,1,2), for a coal sample. The furnace temperature is shown in relation to the ML curve. Residual mass, mass loss and furnace temperatures are plotted as ordinate values, and time as abscissa with the origin in the lower right corner of the page. For ease of reading, script on illustrations is typed parallel to the ordinate. On Figure 3.4 the constant mass lines are drawn across the sheet as they should be, but in some cases, to avoid overcrowding, this rule is violated.



(All symbols refer to the mass loss curve)

(% = percentage value ( ) = milligram)

.... Mass residue curve ---- Mass loss curve

FIGURE 3.3 Comparison of residual and mass loss curves.

Four main stages are identified in Figure 3.4. Main stage one represents low temperature mass losses. Main stage two demonstrates the intake of heat while no mass is lost. Main stage three represents a complex manner of decomposition of the coal while during main stage four, inorganic carbonates and possibly sulphides decompose.

Two time stretches are clearly identifiable over which the mass stays constant viz. AB and DE. These terraces are marked with straight lines as for Figure 3.3. The transition between main stages 3 and 4 is so short that its terminations are so close together that they can be indicated by a single point C. (This case where reactions transgress is very clearly demonstrated for the decomposition of copper sulphate, later). A main stage can thus also be defined by a single (crossover) point through which the partitioning line is drawn.

Four mass fractions can be identified viz. as, iv, tc and mo. These values represent components of a proximate coal analysis, with detail regarding eg the volatiles (iv) furnished. The breaks in the ML curve correspond with specific furnace temperatures which are used to delineate the TG dispersion stages viz. TW, TS, Te and TE.

Figure 3.5 is an example of a more complex ML curve. The subdivisions are made on the same basis as before and symbols for corresponding features are the same but since the coal responds thermally in a different way, additional stage arrangements are required.

Between TX and Te the ML curve drops below the step line (terrace 1). This shows that the mass increased after the low temperature volatiles had been released (dehydration). The temperature where the mass loss, after this gain, again equals the initial mass loss of terrace 1, is noted as T0. This means that main stage 3 must be extended to include second order stages 3A and 3B. For Figure 3.5 TS <> T0 <> TX in contrast to conditions revealed by Figure 3.4 where TS = T0 = TX, because the dormant stage is initiated with a gain in mass prior to the loss of light volatiles.

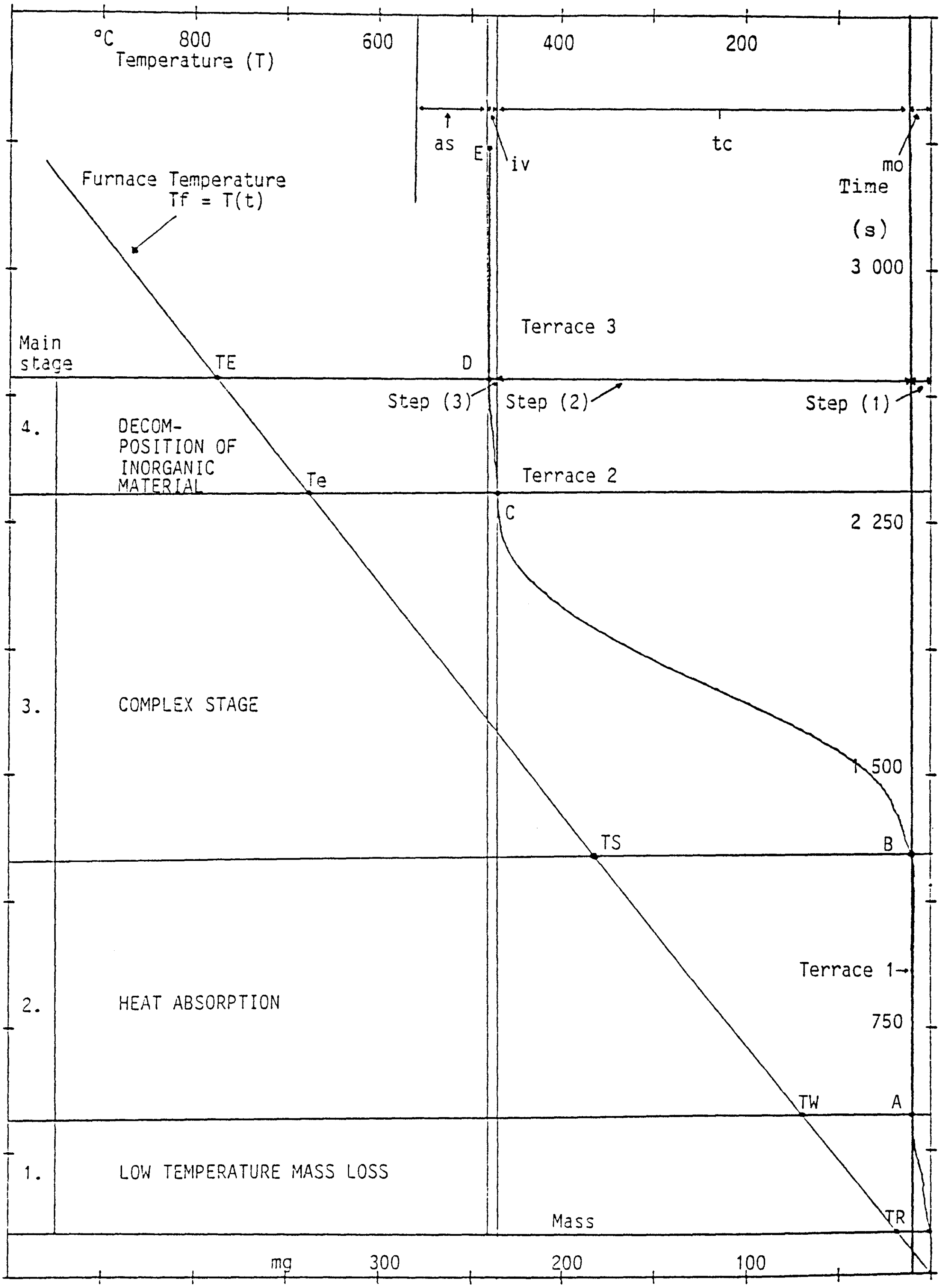


FIGURE 3.4 Analysis of four-stage TG dispersion curve (Original sample mass = 270 mg)

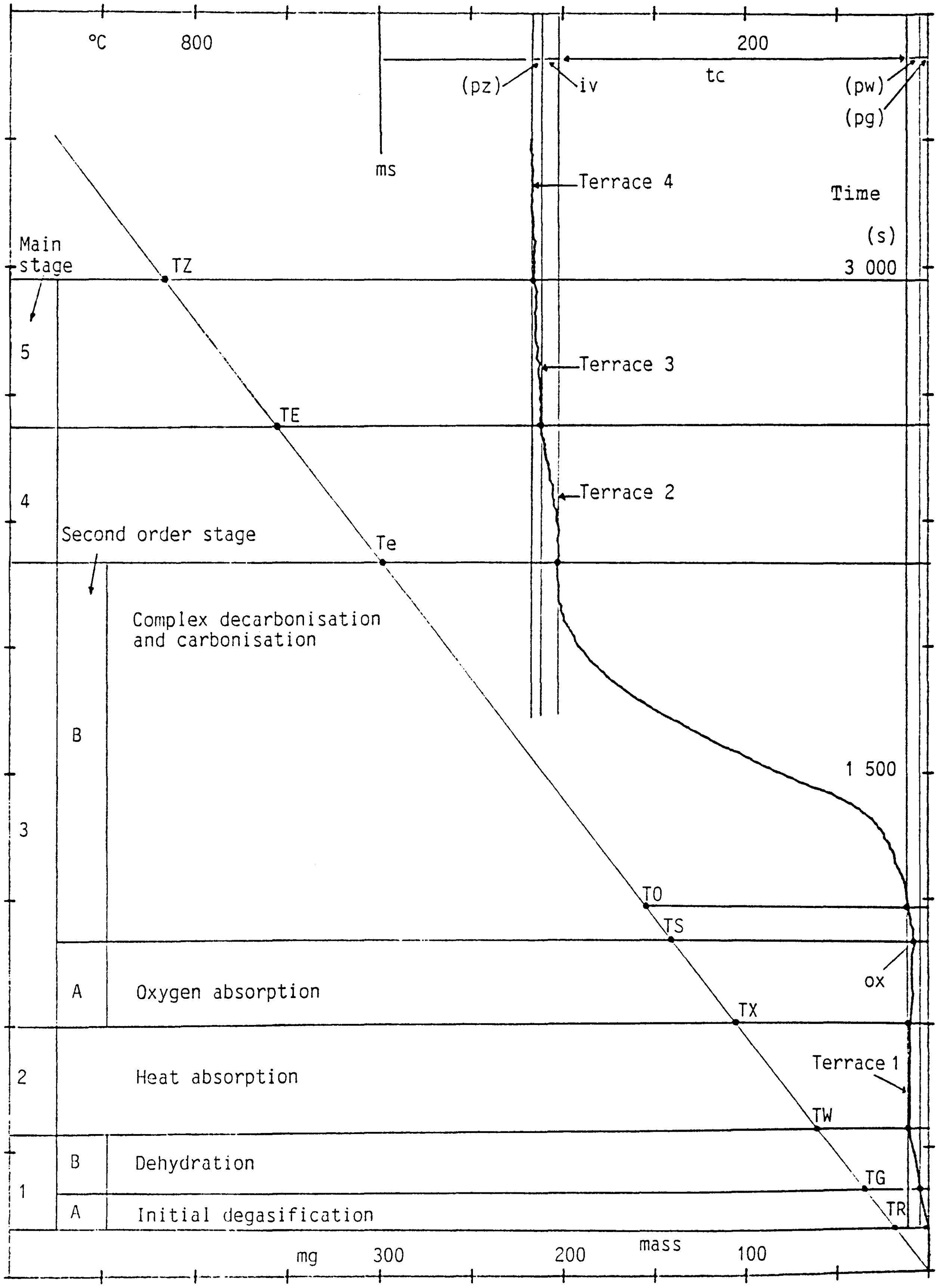


FIGURE 3.5 Analysis of a complex TG dispersion curve (Original sample mass = 300 mg)

Beyond TE Figure 3.5 also shows an additional main stage which is terminated at TZ.

For the first main stage ie between TR and TW a single line step can be identified in Figure 3.5. The temperature limit is indicated by TG. Main stage 1 is therefore also subdivided into second order stages 1A and 1B.

With these variations an additional group of mass loss fractions can also be recognized namely: pw, pg and pz, so that pg + pw = mo = MO (MO = assay moisture %). The gain in mass, ox, is expressed in mg/sample mass. This represents a further addition of detail to the proximate analysis parameters.

3.3.1.2 Combining stable states and DTA data for TG analysis

Figure 3.6 shows the same ML curve and subdivisions as Figure 3.4 but along with the furnace temperature Tf, the near sample temperature Ts, is also shown. The difference between Tf and Ts is presented as the QDTA, or quasi differential thermal analysis curve. This latter curve simply indicates the ranges over which strongly exo- or endothermic reactions occur.

Main stage 3 can be analysed in more detail when Ts or QDTA is also considered. During main stages 1,2 and 4 all possible reactions occur in direct relation to the ambient furnace temperature and are endothermic in nature. This applies to the indexing temperatures TW, TS, Te and TE. However index temperatures TIC and TCO differ in that they do not demarcate stages but fall inside main stage 3. They represent the furnace temperatures between which the process mechanisms are not solely dependent on the furnace temperature but is regulated by a different and usually unknown temperature function Ts, ie the temperature at which the sample burns.

If TIC is considered to be the temperature at which the remainder of a partly decomposed coal sample which has not been deprived of all its volatiles, ie the pseudochar (pc), is ignited and after which sustained burning occurs, then TCO becomes the temperature at which burning, as a self sustained process,

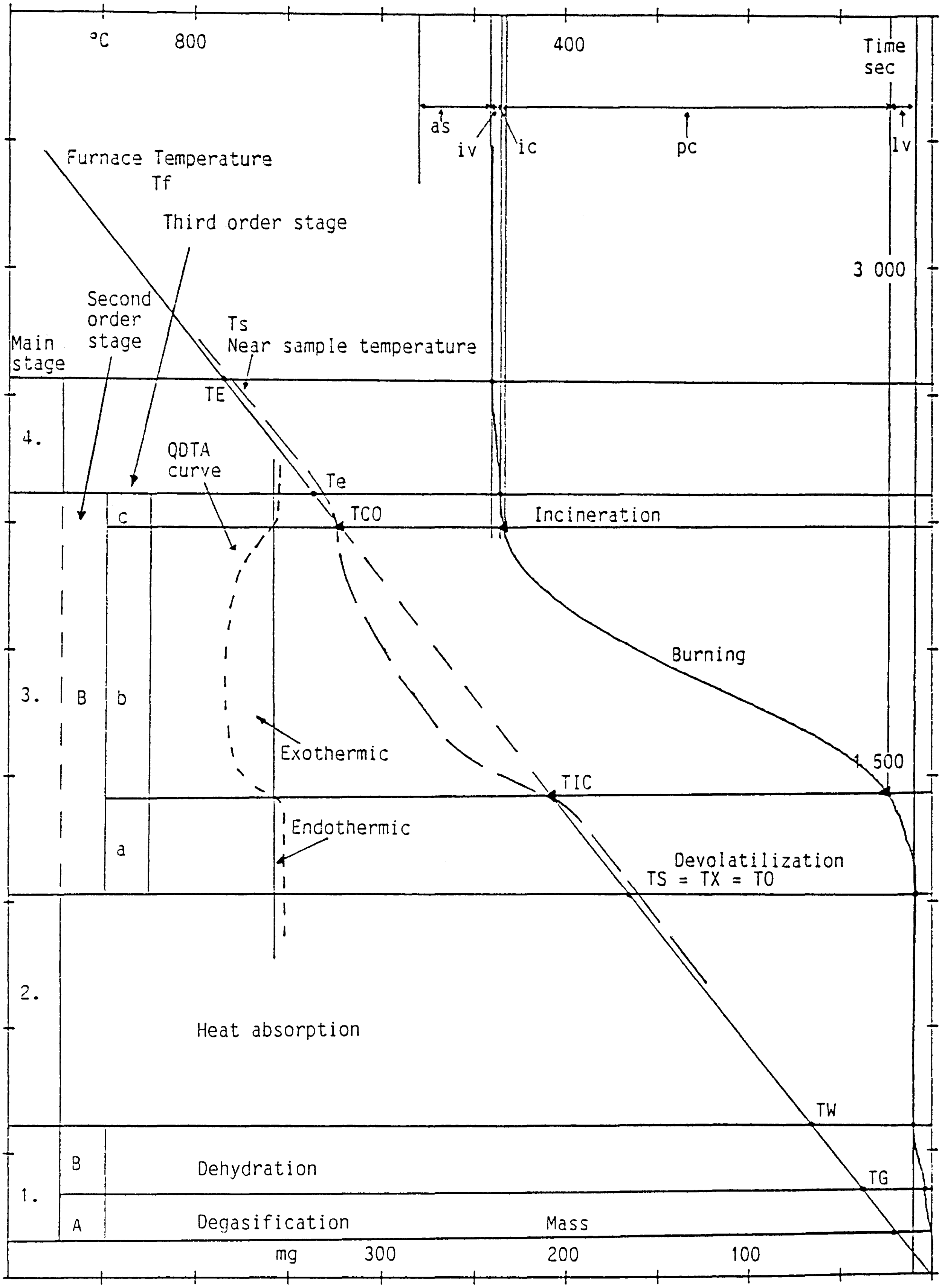


FIGURE 3.6 Adding a third order stage to the TG dispersion curve of Figure 3.5

stops. It therefore follows that between TS and TIC, a third order stage occurs where coal is dissociated without ignition of the reacting substances. This is referred to as decomposition during which a fraction of mass, which has special significance, is liberated. This vapour escapes into the furnace without being ignited, even though oxygen is present, because the ambient temperature is too low. This mass fraction which is released is referred to as the light volatile fraction lv. The interrelationship, tc = mk + pc + lv, is therefore established, (ic = difficult burnable carbon), pc = pseudochar ie char + heavy volatiles plus ash, lv = low volatiles ie liberated before TIC, tc = total combustible material and mk = combustible minerals.

TIC corresponds with the point where the sample temperature rises distinctly above the furnace temperature; TCO is the temperature where the overall furnace temperature again coincides with that of the sample ie the highest temperature at which the pseudochar burns. It should be noted that, in most cases, a small fraction of the carbon is still left at TCO. This fraction is oxidized as a result of heat from the furnace because the QDTA curve shows that the reaction is endothermic.

From Figure 3.6 it is evident that main stage 3 of the ML curve does not reveal any first order stage, therefore, it is the same as 3B. The QDTA curve shows that a third order (burning) stage 3b can however be defined as well as an incineration third order stage 3c. A fully independent third order stage 3a where light volatiles are released, completes this subdivision. Main stage 3 is therefore complex, characterized by carbonisation as well as decarbonisation. The former results in enrichment of the residue in carbon due to loss of volatiles and the latter is characterized by oxidation of the carbon ie burning. Therefore:

3a = devolatilisation (carbonisation)
3b = burning (decarbonisation) and
3c = incineration.

In the more complex case shown by Figure 3.7 depicting a different thermal response, (oxygenation) of the coal, main stage 3 can similarly be subdivided on the basis of QDTA data, viz. devolatilisation, burning and incineration. In this case since

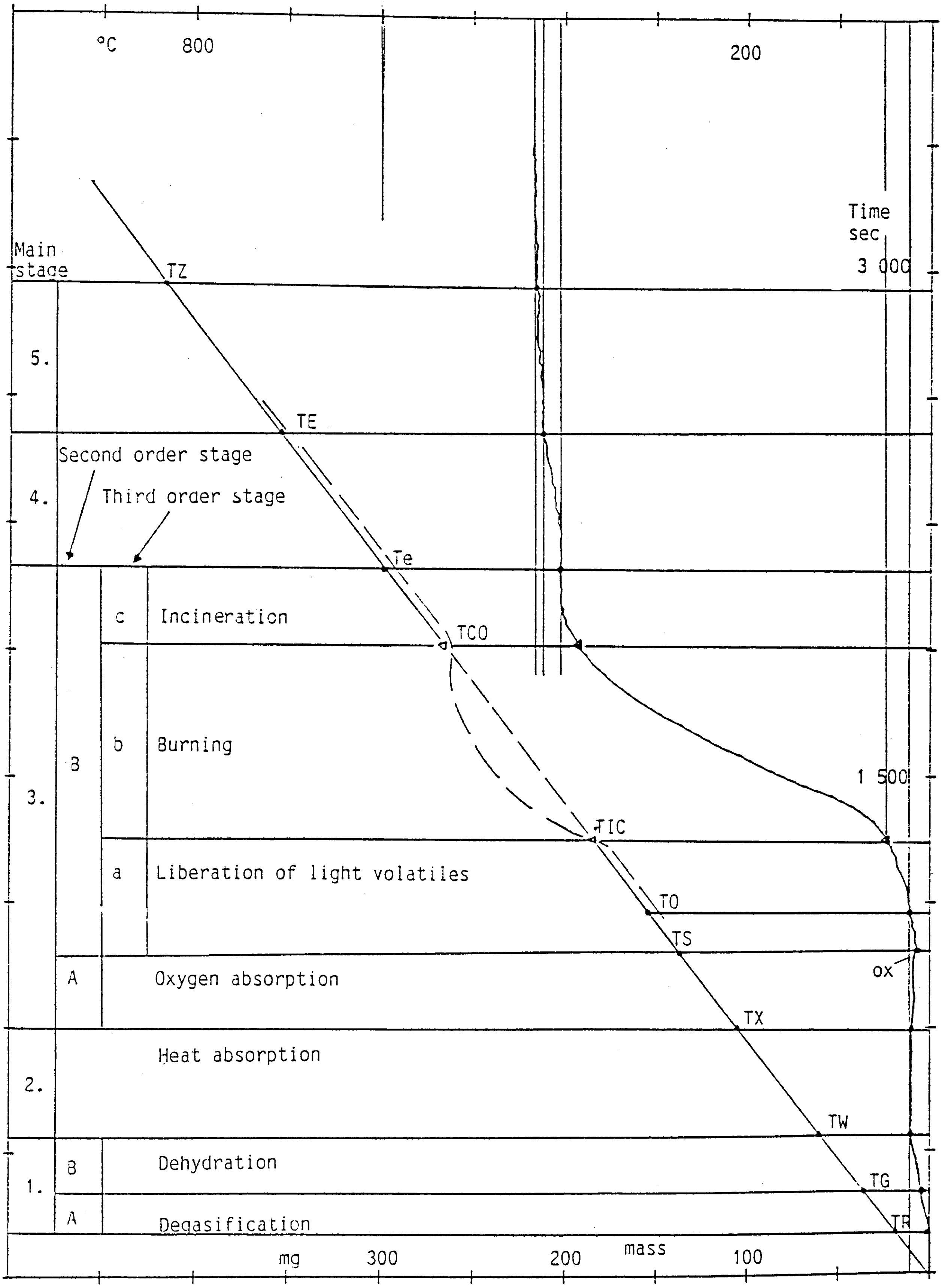


FIGURE 3.7 Adding a third order to the complex setting of Figure 3.5

oxycoal is formed, a second order stage 3A is also present. It is not known when the desorption of the oxycoal commences.

3.3.1.3 The First Differential of the ML Curve (DTG)

The ML curve expresses a relation between cumulative mass lost and time, and therefore can be represented by the expression, m=F(t). Although by physical appearance, the curve looks smooth, its mathematical continuity cannot be guaranteed purely from inspection.

By subdividing the curve into its finite difference elements a function, $F = \delta m/\delta t = \delta F(t)/\delta t$ = the DTG curve, results. Only when $\delta t \text{ --> } 0$, the first derivative of the ML function, $dF(t)/dt$, can be obtained. The process of mechanical differentiation lowers the order of eg polynomial functions, which could reveal features of the derived functions that can be identified by inspection, rather than by the elaborate process of curve fitting, eg a parabola is reduced to a linear function.

On Figure 3.8, which is based on Figure 3.4 the first time derivative of the ML curve, ie the **DTG** curve is shown apart from Ft and Ts. It represents the finite mass increments which are disposed of for each sampling intercept, viz. fifteen seconds for a normal TG procedure, but it can be varied to a lower limit of one second. The unit of the DTG curve is mg/15s, unless otherwise specified, depending on the sampling time. Conversely, the observed ML curve represents $m = \Sigma\delta m$. Ideally, for the limiting case, ie for $\delta m \text{ -->} 0$, the ML curve becomes the integral of the smoothed DTG curve.

Since noise of the mass balance and other disturbances like small mass fluctuations are represented in these values, spurious deviations can occur in the plotted results. To eliminate, with discretion, some of the excessive detail, smoothing techniques are applied.

By averaging the data string values in pairs with different repetition cycles, a well smoothed DTG curve is obtained as shown by Figure 3.8. When minor deviations are ignored, the entire

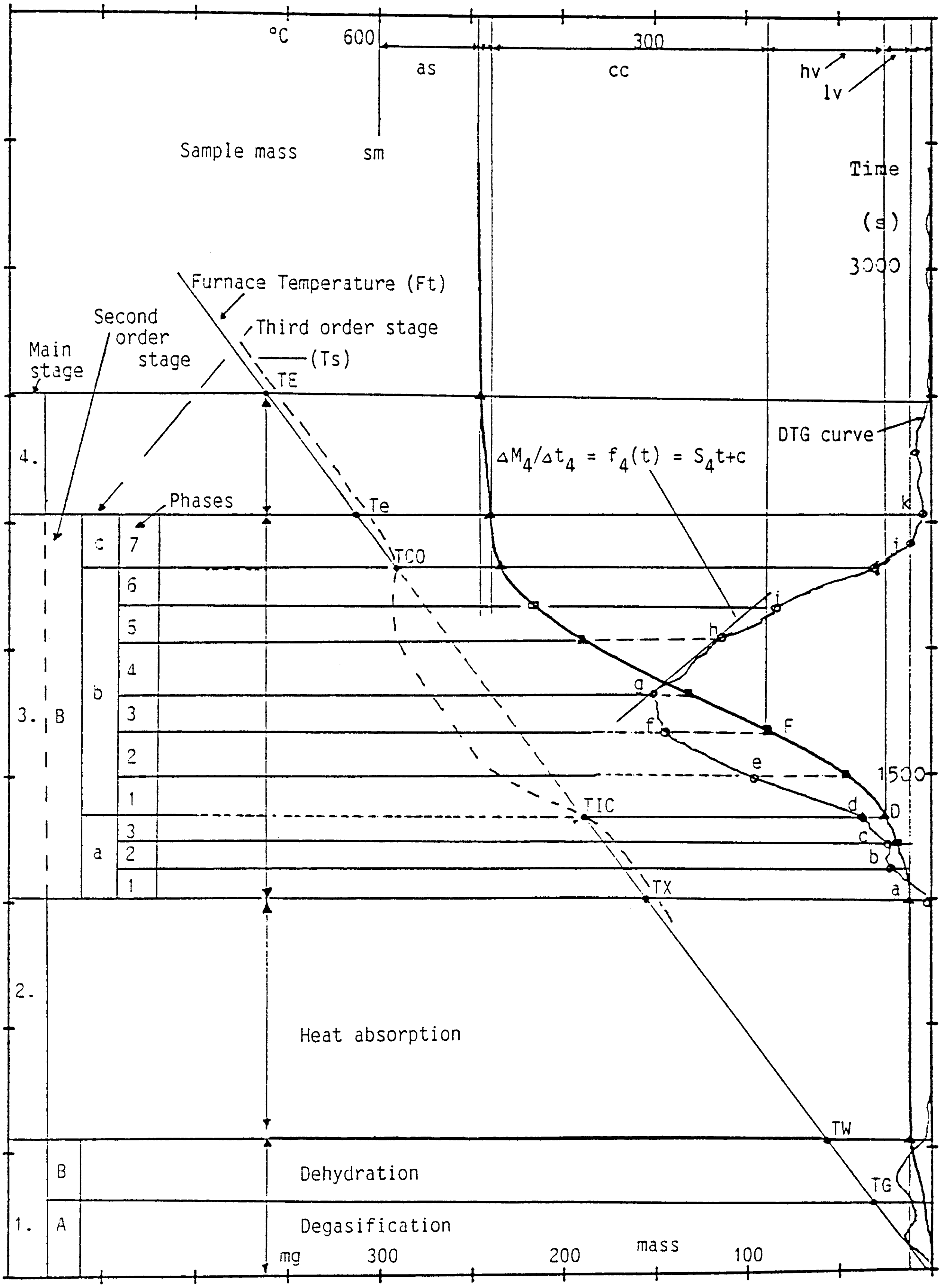


FIGURE 3.8 Adding phases to the third order stages

curve can be considered to consist of intersecting straight line segments eg for the complex main stage 3 they are shown by ab, bc, cd, de etc. Each segment reflects a mass fraction corresponding to a segment of the ML curve. By assuming that the bulk of the remaining combustible volatiles from the organic component of the coal, ie the pseudochar, is released in the phase(s) following immediately after TIC, the peak of the DTG curve indicates when the resulting conflagration ends. Depending on specific analytic control for selection of the best peak for a given coal, the mass lost between the leading peak of the DTG curve and the ignition point of the pseudochar is a very good indication of the high volatiles (hv) which are present. During the remaining, waning burning second order stage a small fraction of combustible volatiles (uv) could be released, but the main remainder can usually be ascribed to the release of volatiles by the clay (ash) or other minerals, excepting the carbonates which release their volatiles during main stage 4. Consequently hv(%) =/= [(F-D).100]/sm. Refer to Figure 3.8 (=/= not equal to).

This suggests that although the ML curve, by inspection, appears to be a continuous monotone increasing function, it really consists of segments of parabola which intersect to form a discontinuous curve. This interpretation follows from the observation that the mean derivative curve consists of continuous straight line segments which identify the stage and phase reactions. The corresponding ML segments which represent the integrals of sets of straight lines, must therefore be parabolas. This provides an analytical basis for the ML curve because, if desired, by picking the various stage and phase discontinuities and integration of the linear functions joining the coordinate points of the discontinuities, a segmented continuous ML curve could be reconstructed. This function could simulate the stochastic observed curve which represents a solution of the actual differential equations which govern the reaction rates ie in analogy with the requirements of the form expressed by equation E1.1 (p 6). The analytical problem of TGA therefore is to find the differential equation, for which the true function of the observed ML curve, is a solution.

From a purely empirical point of view the ML curve can be represented by a series of mass fragments which show up as various "phases" within the burning cycle. Each phase is characterized by a particular "rate of mass loss" function, which slope, eg gh represents $\delta m_4/\delta t_4 = f_4(t) = S_4.t + c$, and $S_4 = d(f_4(t))/dt$. (Figure 3.8). According to Solomon, (1981, p 66), "These rates characterize the thermal decomposition of the various functional groups. They depend on the nature of the group but appear insensitive to coal rank".

On the basis of the discontinuous nature of the ML curve the use of its overall form feature as a solution to the expression of the normal rate of reaction expressions, such as E1.1 (p 6). Daniels, 1972 and Blazek, 1973 is not advisable.

The simple TG curve (Figure 3.8) shows how the phases are distributed through the second order stage 3. Some of the phases have been identified in terms of real processes such as, eg 3Bb1 which represents the first accelerated mass loss which occurs immediately after ignition of the pseudochar. Most of the other phases can as yet not be explained. The first and/or second phases after ignition, can be used to estimate the limit of significant volatile release. Hence, hv can be identified. The specific choice depends on the nature of a particular coal, eg vm is established through the application of devolatilization techniques such as S(1,1,3). The association to be established is tc = lv + hv + fc (+ mk), tc = total combustibles ie volatiles plus solids. (Combustibles from mineral compounds mk, are ignored for the present.) The normal combustible char is indicated by cc.

Figure 3.9 shows how the phase structure fits into a complex dispersion setting. The complete relation between mass fractions which can be identified and how dispersion analysis provides substantial detail regarding proximate analysis parameters, are shown.

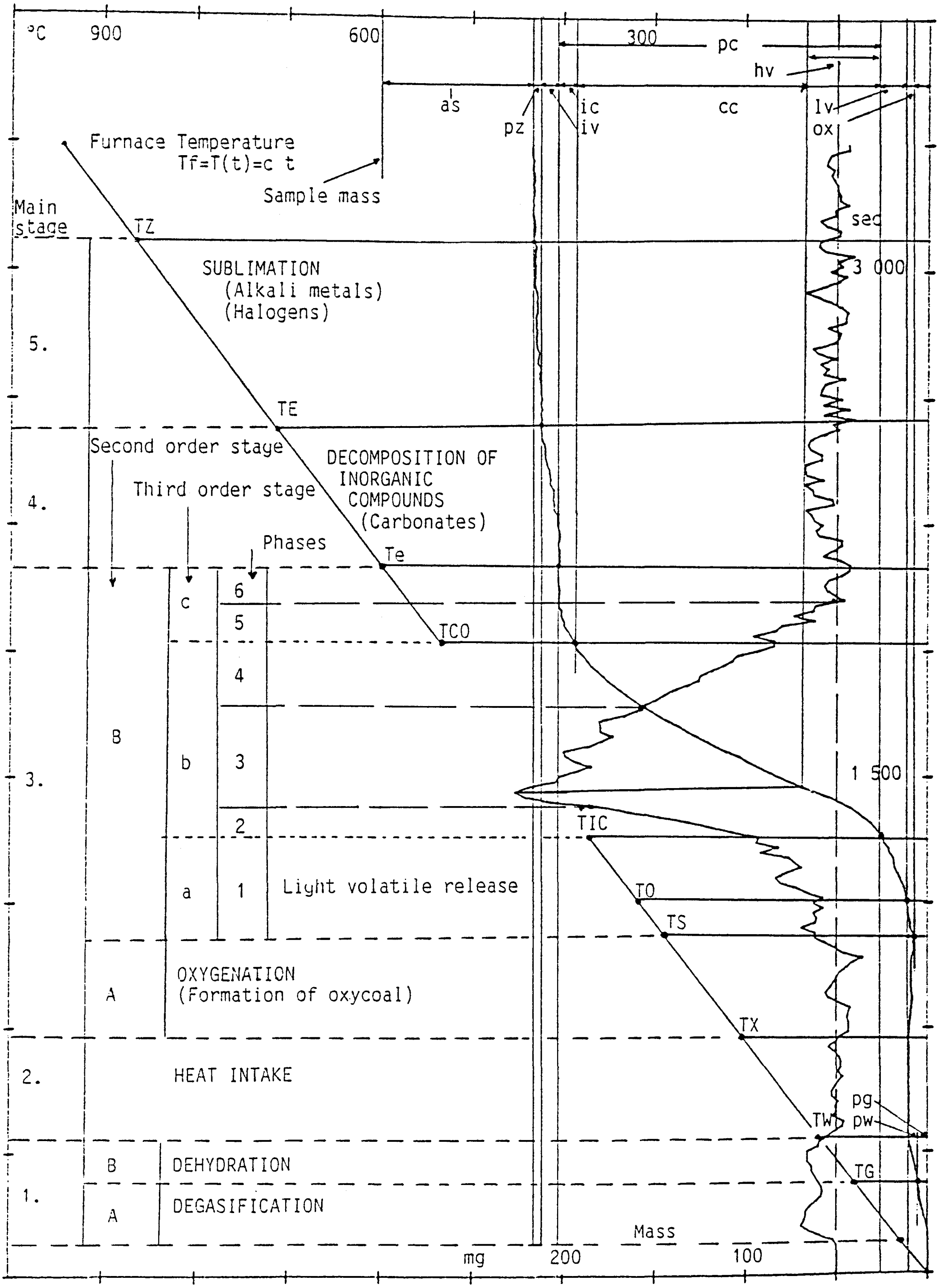


FIGURE 3.9 Adding phases to the second order stages of a complex TG dispersion curve

3.3.1.4 The Second Differential of the ML curve (D2TG)

Figure 3.10 shows the computed DTG curve and its slope variations within the different stages. The DTG curve is not smoothed so that as much detail as possible is retained. The smoothed, ie mean, DTG curve is derived from the actual DTG curve as a shifted idealized straight line. It is shown on Figure 3.10 as intersections of a series of straight line segments to show how it originates.

If it is accepted that the first derivative of the mass loss function within a reaction phase is linear, then its derivative, ie its slope, is a constant, indicating that the rate of, the rate of mass loss, does not change within a phase.

This function is a stepped curve designated as the D2TG curve (Figure 3.11). For the thermogram as a whole a series of definite waxing and waning reaction phases will be present. The most significant of these occur in the carbonisation-decarbonisation stage B; commonly nine of these phases occur within this stage but variations are possible.

A further characteristic is that the reaction phase which follows immediately after TIC usually has the highest peak value and it is referred to as the D2TGi. In a physical sense D2TGi represents the highest rate of reduction in mass. Since TIC represents the ignition temperature, it follows that D2TGi is a quantitative measure of the propensity for burning of the coal or of its "reactivity" with respect to oxygen at elevated temperatures.

In order to define the reactivity of burning of coal in connection with TGA some of the other usages of the term need to be considered.

Chemical affinity is defined in terms of the free energy change dF, which results from a given reaction: (Moore, 1956, p 71):
dF = F (products) - F (reactants): (F = free energy).

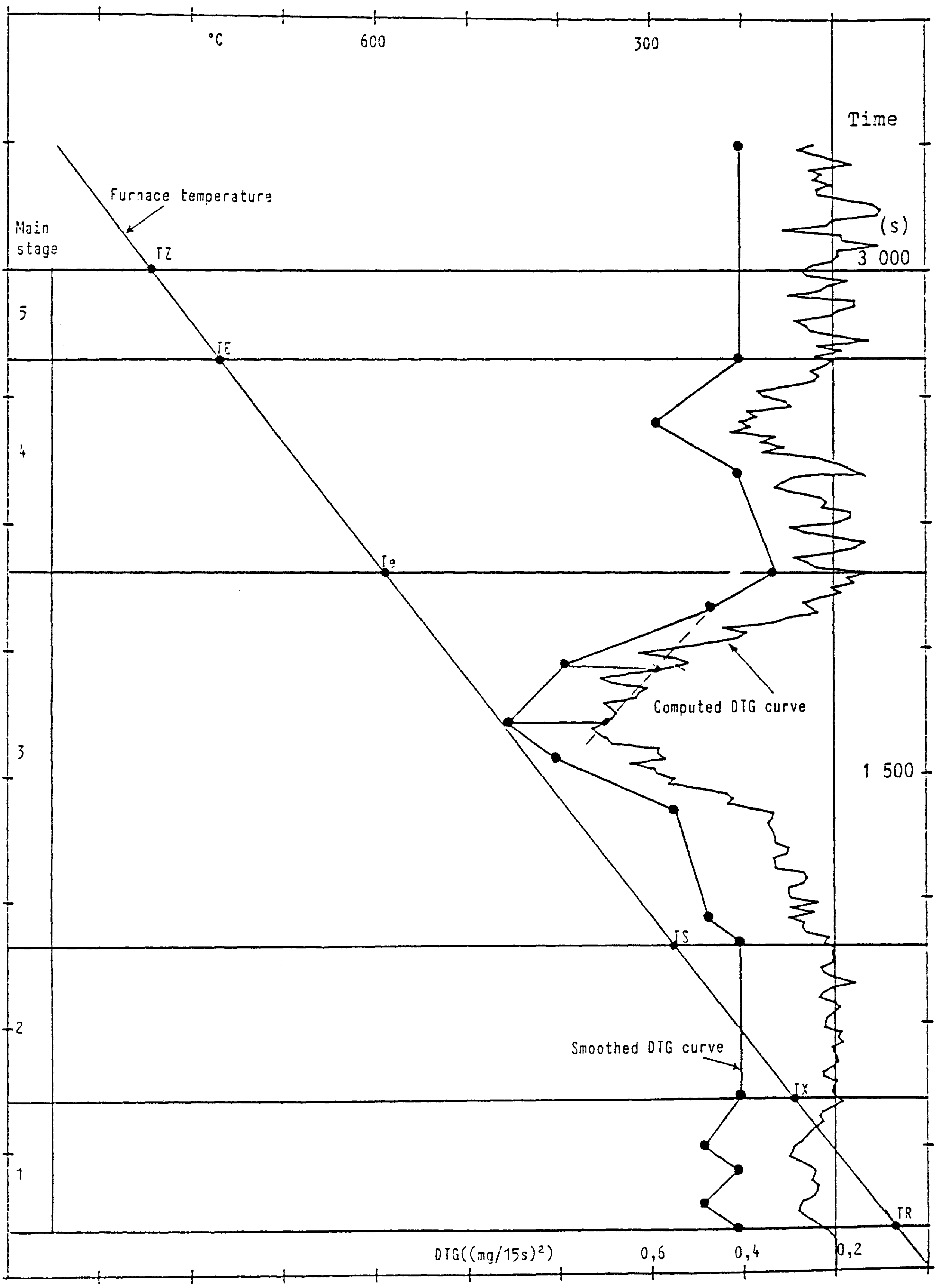


FIGURE 3.10 Deriving a smoother DTG curve for purposes of analysis

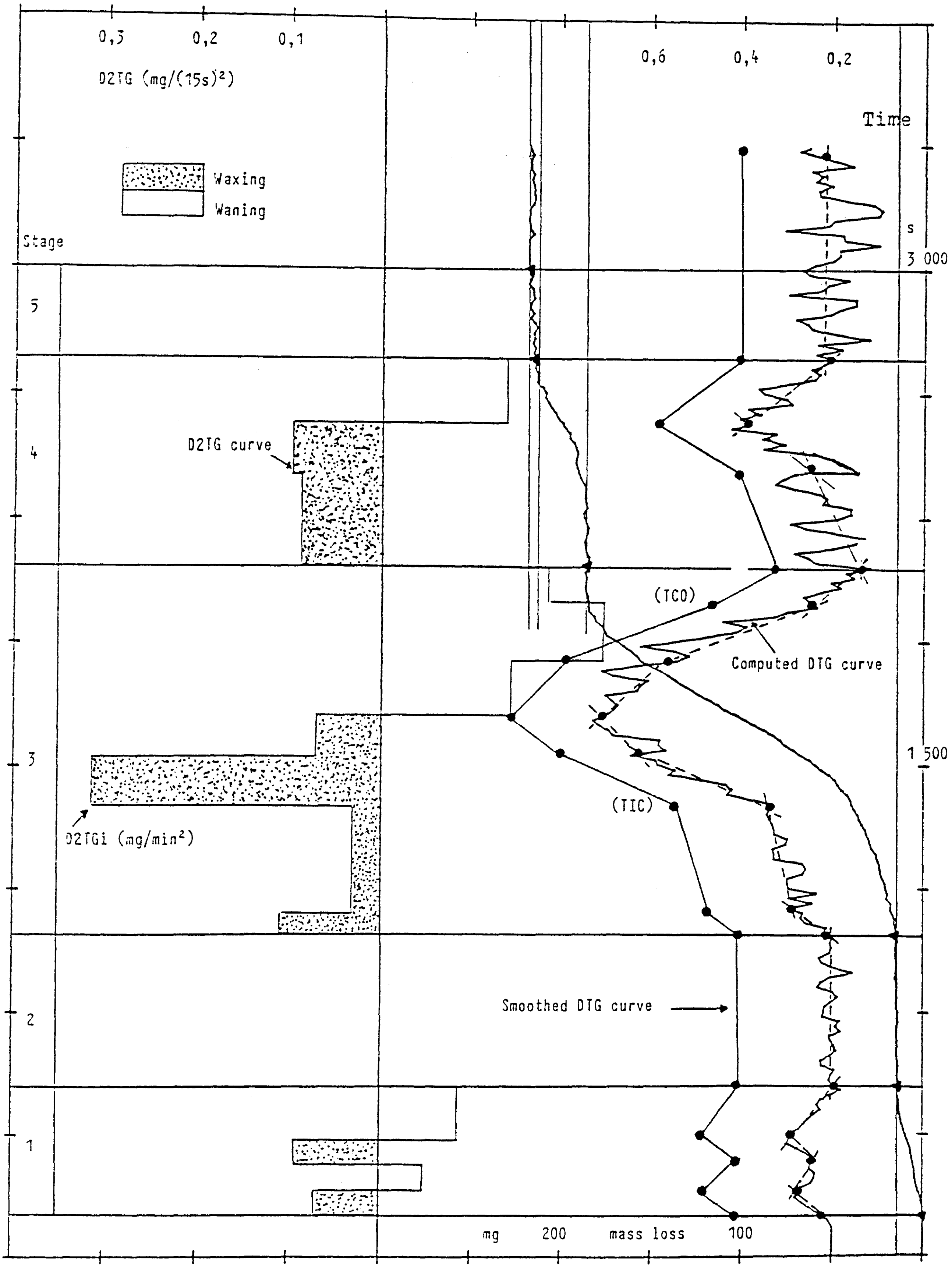


FIGURE 3.11 The releation of the D2TG curve to the Mass loss and DTG curves

According to Lowrey (1963, p 521), "reactivity" is somewhat loosely used to express the ability of a coke to react with oxygen, carbon dioxide or steam.

Van Krevelen and Shuyer (1957, p 312-332) describes the reaction of coal with oxygen in different categories inter alia by microscopically measuring the width of the reaction rim that forms around a coal grain. They discuss other parameters including the absorption of pure oxygen in conjunction with DTA and TG experiments and conclude that the measured activation energies are characteristic reactivity parameters (p 325).

A really practical approach for determining the relative propensities for burning of different coals was presented by Pollock et al (1983, p 14). They required a means for estimating the reactivities of coals in free air for purposes of furnace design.

Chars prepared from different coals were heated to 710°C in a nitrogen atmosphere. Air is then introduced to induce burning. The recorded mass loss is measured as a function of time and the data are plotted (Figure 3.11a). In this manner the aptitudes of chars with different structures are tested for burning without allowing them to become saturated with air after cooling.

It was found by Pollock et al (1983) that char burn out curves which fall to the right of that of a standard reference coal, viz. curve B, indicated that a special design of the furnace was necessary to effect complete burn out of the coal. The slope of the mass loss curve thus becomes a measure of comparing the thermal response of different coals.

The second differential of the ML curve immediately after ignition of the pseudochar (TIC), designated previously as D2TGi, quantitatively expresses the propensity of the pseudochar to burn in air. The advantage of using D2TGi is that only one test, which provides other information as well, is required to determine the reactivity of the char with respect to burning. D2TGi can also be directly compared for different coals.

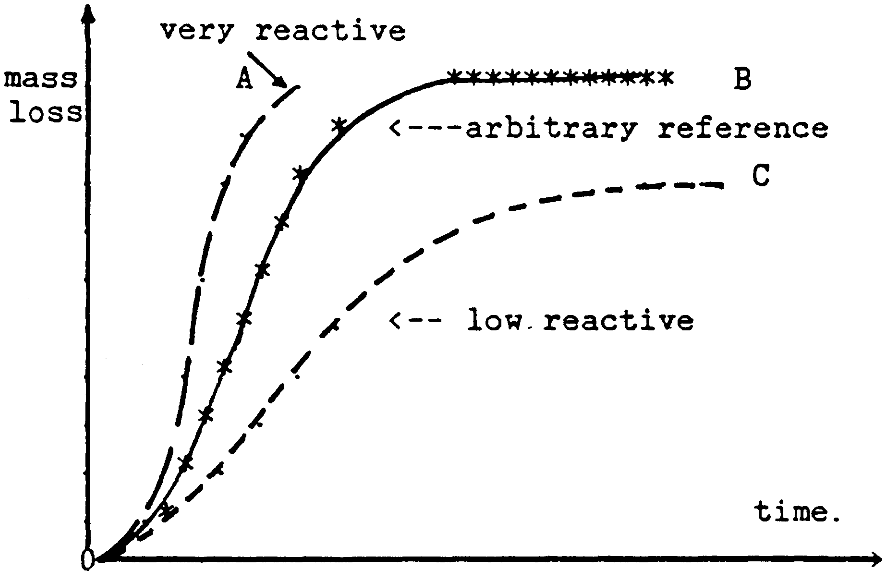
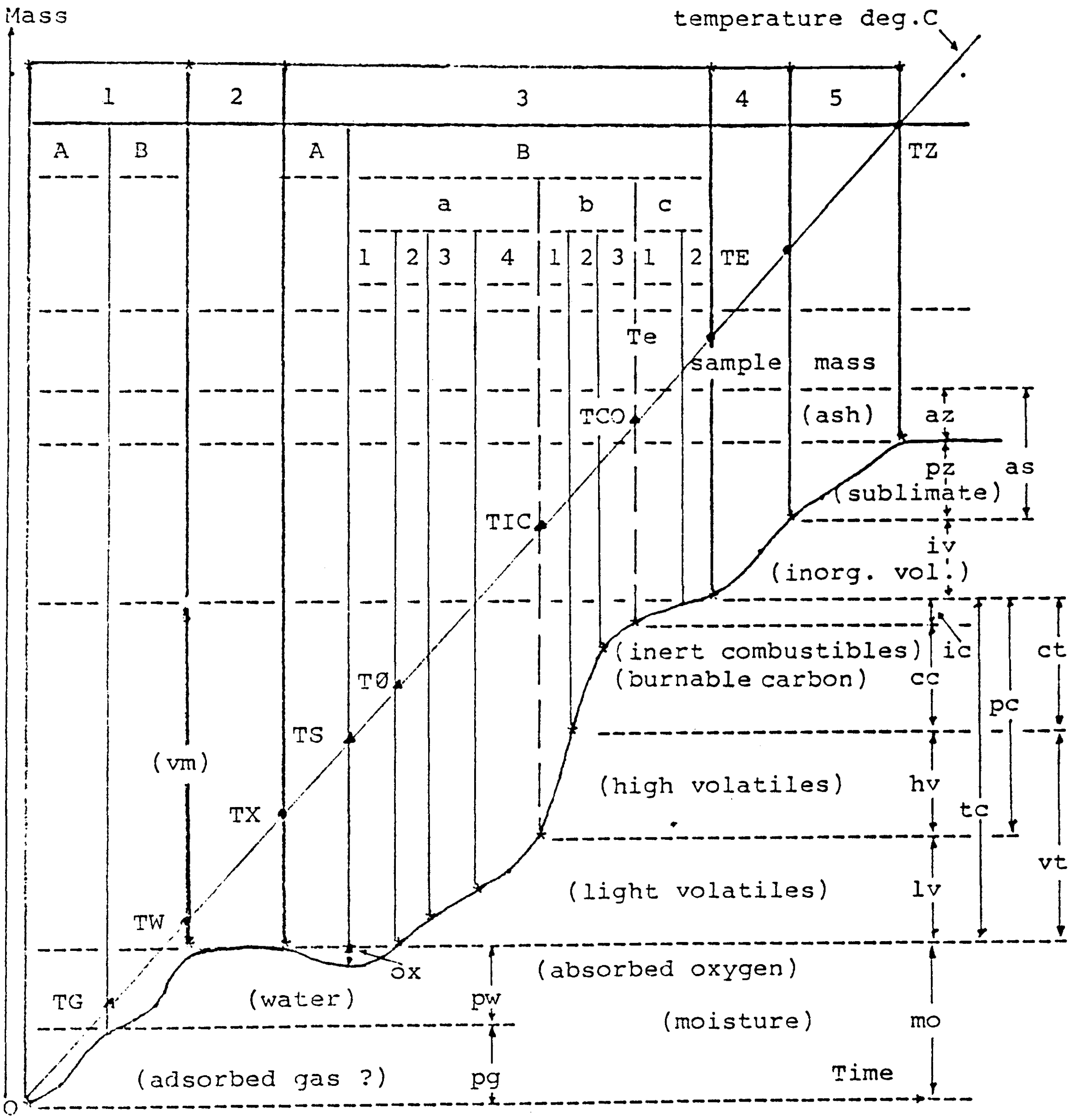


FIGURE 3.11a Combustion Engineering's reactivity tes
(Curves are schematic)

3.3.2 Discussion of the significance of the reaction stages in a dispersion analysis

The analysis thus far, indicates that a set of quasi-proximate analysis values, very similar to the standard parameters but with detail added can be derived from TG dispersion results, by assigning physical connotations to the specific mass fractions on the mass loss curve. The TG parameters are determined on a natural basis, instead of an air dry basis because the TG samples are not acclimatized before processing. The overall results can however be assumed to be comparable to the standard (adb) laboratory proximate analysis values. Small type symbols will be used to distinguish TG derived values from standard values.

Figure 3.12 schematically shows how subdivision of the ML curve is related to diagnostic mass fractions which can be combined to produce a set of percentage parameters which correspond reasonably well with their standard proximate analysis equivalents indicated by large type symbols in the related equations. The TG derived (quasi) proximate percentages, are subdivided on the basis of TG diagnostics and these need not necessarily correspond with other subdivisions, eg total inorganic volatiles (ti) (not possible to show in figure 3.12), normally include volatiles from clays and other minerals, while for TG, (iv) indicates essentially carbon dioxide from carbonates and sulphur dioxide from sulphides. A way has yet to be found to determine where the volatiles from eg clay minerals (mv), reside; ie with the light or heavy volatiles, or both. This was already partly checked experimentally by recording the TG dispersion response of pure kaolinite samples which showed that a ML curve similar to that for coal is displayed and that TS and TE ranges from about 400 to 550°C, which places it within the normal burning range for coal ie second order stage 3Bb2 to 3 as shown by eg Figure 3.9. This is confirmed by the DTA thermograms of Mackenzie (1976) which show that OH, from kaolinite is liberated as H_2O at approximately 500°C. If the kaolinite of the sample is known eg through XRD (x-ray analysis), the incombustible volatile yield for high kaolinite coals can be expressed as a function of the ash content: TG analysis showed that pure kaolinite yields between 10 and 13 percent volatiles.



pw + pg = mo = MO%

az +pz = as =AZ%

iv + lv + hv = vm = VM%

ic + cc = fc = FC: lv + hv + fc = tc = lv + pc (%)

cv = ((33,04 . vm) + (32,9 . fc))/100 MJ/kg

FIGURE 3.12 A schematic outline of prominent stages and the associated % parameters for a dispersion test.

For coal studied which contained > 90% kaolinite in the mineral matter the formula:

$$vk = (vm - ti) = vm - (iv + mv), \text{ holds.}$$
$$vm = lv + hv + uv + ti = lv + hv + uv + iv + mv + me \qquad E3.0$$
$$ho = vm - lv$$

where: vk = combustible volatile %; vm = all volatiles %; ti = total unburnable volatiles %; iv = incombustible volatiles originating from carbonates decomposing above about 600°C %; mv = volatiles from clay minerals (kaolinite) %; uv = an unknown fraction either combustible or incombustible which could originate from sources thus far unidentified; me = volatiles from combustible inorganic compounds; ho = heavy volatiles and lv = light volatiles.

All the outlined components except uv can be determined by means of TG techniques. Provisionally the extended quasi parameters are strictly for comparison with other TG equivalents.

Some difficulty is experienced with the determination of VM and FC, both on account of standard laboratory specifications and in terms of fundamental definitions for the quantities which are sought. A further problem arises from the situation that it is desirable to derive all required data for a TG based quasi-proximate analysis, <u>from a single experimental operation</u>.
To attain this objective the precision limits for TG derived parameters must be relaxed and corresponding nomenclature established otherwise unjustified comparisons between observed quantities could be made. The values for hv and ho are under some conditions acceptable as the same quantities or mv and me, being small quantities, can sometimes be disregarded.

A point to observe is that TG proximate parameters are not "wrong" because they differ from laboratory determined values. They differ because they are measured under different conditions and therefore represent different entities to those measured otherwise. These differences could convey information if properly interpreted for compatibly observed data.

TG procedures can be adopted whereby quasi-proximate values corresponding to standard ones are obtained (Cumming <u>et</u> <u>al</u>, 1982).

This defeats the main objective of acquiring through a single experiment maximum information about the response of coal to applied heat and the proximate parameters are regarded as a bonus.

If standard proximate analysis is required it is only necessary to program the apparatus so that the specifications are met separately, for moisture, ash and volatile matter determinations. This would imply three experiments viz. S(2,1,2), S(3,1,2) and S(3,1,3) respectively.

3.3.2.1 <u>Direct information derived from the various stages</u>

Apart from the quasi-proximate parameters and diagnostic temperatures shown by Figure 3.12 an interpretation of the physical-chemical transformations which are likely to occur during each stage, is as follows:

MAIN STAGE 1

The first mass fraction which is disposed of, is usually ascribed to the loss of moisture. The determination of moisture is based on this assumption since the sample is heated to slightly above the boiling point of water. From the TG data it is clear that two stages of mass disposal are involved between room temperature (TR) and TW. The latter temperature is usually around 115 - 130°C while TG is usually around 60°C, ie where the first mass release usually terminates. On account of this the range for low temperature mass loss, ie main stage 1, must be subdivided into two second order stages.

Although no proof can be furnished at present, it could be possible that the first mass which is released (second order stage 1A), may represent gas and surface moisture which is adsorbed physically on the coal.

Moore (1956, p 514) describes physical adsorption as distinctly different from chemisorption although both are essentially surface phenomena. The former represents loosely surface bonded molecules which involve energies of the order of hundreds of joules per mole and involves reversible processes. Chemisorption involves strong binding forces comparable to those leading to chemical compounds.

Second order stage 1A is important, because any possible parameter which can relate TGA and spontaneous combustion should be detectable within this stage where the low temperature reactions occur.

The mass released between TG and TW, ie second order stage 1B, can hardly be anything else than water. The TG therefore bears out that either two kinds of water or gas and water combined are released at the start of TG dispersion. It follows that:

adsorbed gas + intrinsic water = moisture ie MO

Marik-Korda (1983, p 194) claims for studies of European coals, using a special technique which can only detect intrinsic water, that: "However, as shown by the thermoanalytical curves, on heating these coals to a temperature between 150 and 200°C, an additional 0.8 to 3.0% moisture is removed from them." This is not corroborated by current TG results which show that above about 135°C no further loss is encountered ie a stable stage is entered.

MAIN STAGE 2

Between TW and TX no mass is released and the sample is simply heated to a higher temperature. It cannot be claimed that no reactions occur, but only that no mass is being disposed of during the processes which may occur. The temperature range between TW and TX can vary appreciably ie main stage 2 is variable depending on whether the coal is susceptible to the formation of oxycoal or not. When the coal does not absorb oxygen TX coincides with TS and no second order stage 3A is formed.

MAIN STAGE 3

If main stage 2, (Figures 3.9 and 3.12), is characterized by a gain in mass the complex decomposition, main stage 3 is initiated at a lower temperature than TS and must be extended to incorporate second order stage 3A which adds the initial process of oxycoal formation (chemisorption) ranging from TX to TS. The maximum amount of oxygen bonded by a 300 mg sample of coal is about 10 mg which is reflected as a gain in mass and it terminates at TS. Thereafter mass reduction commences again and continues until the previous dehydrated level is crossed at the temperature T0.

This aspect was discussed by van Krevelen and Shuyer (1956, p 317-319), quoting Oreshko who carried out TG work in this regard. The results of Oreshko, according to a graph furnished by van Krevelen, op cit p 316, are almost identical to the ML curve of Figure 3.7. Oreshko's third stage, which corresponds to the present second order stage 3A, was interpreted as due to the formation of oxycoal. If this is correct the observed increase in mass must be due to the absorption of oxygen from the air. The actual mass is measured at TS and noted as a mass fraction, ox, in milligram for the standard 300 mg sample.

Second order stage 3B, is defined by temperatures TS to Te or TE, since Te=TE when main stage 4 is absent.

Carbonisation-decarbonisation second order stage 3B is complex and requires further subdivision. The coal first releases volatiles leaving a carbon enriched product, (pseudochar), then burns to consume carbon and associated products to leave a decarbonised residue.

Second order stage 3B, (Figures 3.9 and 3.12), consists of three third order stages, 3Ba, 3Bb and 3Bc, which are marked by the diagnostic temperatures TIC and TCO, both of which can always be identified in terms of the start and end of the highest exothermic reaction ie burning. A distinct rise in the increase of mass loss, (Figures 3.8, 3.9 and 3.11), which corresponds with the rise in sample temperature after TIC, corroborates that ignition of the partly decomposed coal occurred. TCO likewise follows after a similar steep decline in the mass loss rate was attained, (Figure 3.11). It is therefore not essential that the sample temperature be recorded in order to identify these two points on the ML curve; they can be identified from the DTG curve.

The fraction of mass, (Figure 3.9), which is given up between temperatures TS and TIC represents volatiles which are released without ignition. A notable endothermic reaction may sometimes accompany the third order stage, 3Ba. After ignition at TIC, distinct glow-burning can be observed. During the temperature range TIC to TCO, ie third order stage 3Bb, the rate of mass loss can vary appreciably while disposing a fraction, pc of the partly devolatilised coal, ie the pseudochar burns out. After TCO, ie third order stage 3Bc, mass is lost at a very slow rate. The oxidation process is forced, through the heat of the environment, (incineration), on this fraction ic, of the highly carbonized coal residue, which could resemble coke or possibly even graphite which only burns with difficulty. The char, ie carbon and ash essentially formed after the first peak of the DTG curve, thus consists of easily burnable carbon and inert fractions, respectively.

MAIN STAGE 4

Temperatures Te to TE identify the stage where inorganic materials start to decompose because there can hardly be any organic material present due to burn out during third order stages 3b and 3c. Main stage 4 is absent from the dispersion ML curve for -70 mesh sugar char, because there is no decomposable inorganic material (carbonates) present. It is therefore reasonable to expect inorganic materials, which are present in other chars, to decompose at this stage. Dispersion analysis of pure calcium carbonate and calcite revealed that both these materials start to decompose around 580°C which is in agreement with the recorded information. These temperatures should vary with the composition of the inorganic material which is present eg sulphides or carbonates. For Figure 3.9 calcite was positively identified and the (iv) temperature matches that for calcite. Also refer to Figure 3.32, (p 108) which shows how calcium carbonate decomposes.

MAIN STAGE 5

The last stage is marked by TE and TZ. The loss of a small percentage of mass pz, can be identified clearly on the ML curves from some coals. It is always absent from ML curves of pure carbons in the form of char, but it corresponds well with the observed start temperature TS (800°) for graphite. Indications are therefore that main stage 5 is most likely associated with the inorganic or highly metamorphosed residue of coal and may tentatively be ascribed to a state where high temperature sublimation of metals or decomposition of halogen compounds or perhaps boron compounds, may occur. It is possible that eg phosphorous compounds may evaporate at this temperature range or that some of the metallic atoms are volatilized. At present no positive information can be furnished to this effect but further investigation could be fruitful because it is not unlikely that the materials responsible for furnace fouling may be identified at this temperature range.

3.3.2.2 <u>A decomposition model for coal</u>

In order to relate these TG diagnostics to practical burning of coal, a global mechanism for thermal dispersion must be outlined and certain concepts defined, in particular regarding the reactions and products concerning the complex carbonisation-decarbonisation main stage 3.

This will be done using the model formulated by Solomon (1981, p 62-69) for US coal (Figure 3.13). This model may not be applicable to other coals, but the major principles are accepted to formulate wider generalizations. To facilitate reference to aspects of current importance various subscripts are added to the model depicted in the two diagrams of Figure 3.13. Diagram 1 represents the hypothetical coal molecule and diagram 2 the molecule in its partly decomposed state ie after thermal excitation induced disruption of the linking chains eg 1 to I, 2 to II, 3 to III etc. The model does not include oxidation of the aromatic clusters which constitute the tar ie S(1,1,3) seems to apply.

a. For purposes of analysing its decomposition, coal can be visualized as consisting of groups of aromatic and hydroaromatic ring clusters ie (1), (2), (3), (4), (5) diagram 1, possibly linked by relatively weak aliphatic bridges eg 1, 2, 3 and 4 (Diagram 1).

4. SOLOMON *Coal Structure and Thermal Decomposition* 63

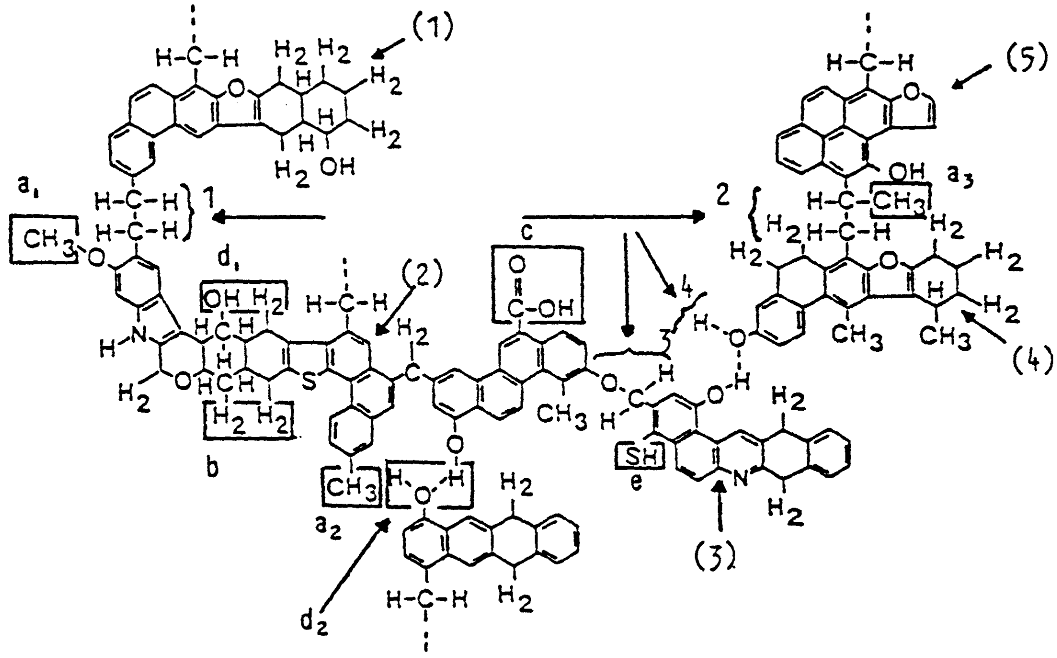


Figure 1. Summary of coal structure information in a hypothetical coal molecule

Diagram 1

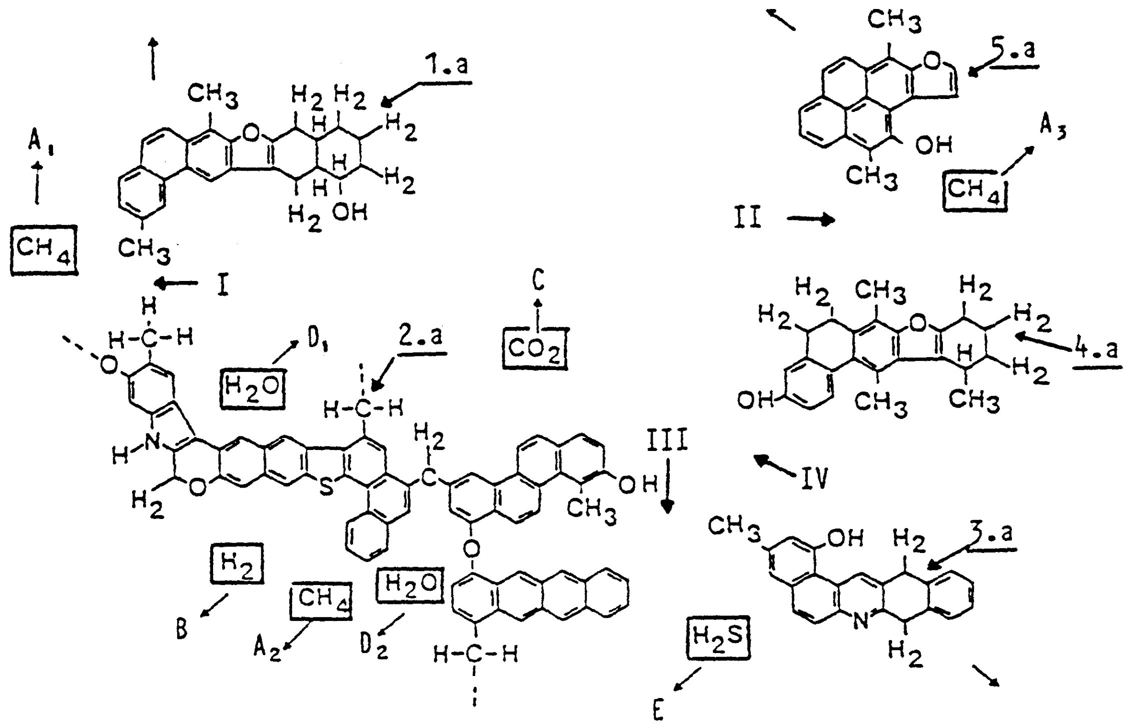


Figure 2. Cracking of hypothetical coal molecule during thermal decomposition

Diagram 2

FIGURE 3.13 The thermal decomposition of coal, based on the model of Solomon (1981)

b. Carboxyl appendices to the ring complexes, ie c, in diagram 1 are responsible for yielding of carbon dioxide ie C in diagram 2, during thermal stimulation. Other products such as oxygen ie d_1 vs. D_2, can also be related to specific structures within the overall complex such as eg ethers, but complete detail is presently not relevant.

c. Decomposition, most likely starts by breaking of the aliphatic linkages ie 1, 2, 3, etc. which bind the aromatic clusters together (Diagram 1). This releases the clusters to form tar ie the aromatic clusters <u>1a</u>, <u>2a</u>, <u>3a</u>, <u>4a</u> and <u>5a</u> in diagram 2, and is known as cracking. Tar therefore represents unbonded aromatic clusters in free association with each other.

d. Cracking of the link chains a_1, a_2, etc., produces the light gas molecules such as methane ie A_1, A_2 and A_3 in diagram 2.

e. The aliphatic structures break up at low temperatures while the ring clusters disintegrate at high temperature, which results amongst others, in the release of hydrogen ie b in diagram 1 to B in diagram 2.

f. With extensive decomposition beyond the processes illustrated, the aromatic clusters, stripped of hydrogen, yield carbon (char) which becomes more graphitic at high temperature because the fundamental aromatic carbon ring lattice is retained by the hydrogen stripped carbon groups.

g. It appears logical to surmise that "fixed carbon" as determined by proximate analysis conditions, represent essentially "the skeletons of the aromatic rings". Solomon also quotes van Krevelen and Shuyer (1957), as being in support of this concept.

To some degree the TG dispersion process, S(1,1,2), represents a transgression from S(1,1,1), ie pyrolysis in absence of air, which corresponds to S(1,1,2) at low temperatures, (T < TIC) to a system of free burning followed by forced heating incineration. External oxygen is always present to react with a partly decomposed product consisting essentially of aromatic complexes, but still containing volatiles. These volatiles are referred to as heavy volatiles (ho) and the carbon which evolves from it as char (cc or ct, Figure 3.12).

In Solomon's analysis the fact that coal consists of macerals which have different compositions and molecular structures was not considered. As far as burning of given coal is concerned it is important to establish how and from what maceral groups, its light volatiles originate and over what temperature range its high volatiles (hv) are released, because the light volatiles should control inflammability while the high volatiles should influence reactivity or propensity for burning.

It is beyond the scope of the present study to extend observations to the analysis of gases which are released during dispersion. The results published by other observers are presented to show what can normally be expected.

Figure 3.14 is a schematic presentation of the results obtained by Juntgen et al (1979, p 272, 274) for gas formed when European coals, ranging from anthracite to high volatile types, are heated. The spread along the ordinate indicates where maximum release rates occur while the abscissa shows the approximate temperatures where the reactions start and end.

The range of the temperatures, TS to TCO, normally defining main stage 3 of a dispersion test on SA coals, is also shown. The formation of the products between TIC and TE is reasonably in accordance with expectations but release of ethane around 200°C has not been observed in dispersion analysis as a mass decrease, for SA coals. The formation of hydrogen, nitrogen and carbon monoxide for temperatures higher than about 850°C can hardly be explained in terms of the decomposition of organic residues from SA coals. About the release of H_2, CO, and especially N_2, the authors, (op cit, p 275) remark that the releases are not finished even at 1000 °C and that the hydrogen, oxygen and nitrogen atoms are included in the coke structure with high bonding energy.

In the light of the combined information from Solomon's model and Juntgen et al's pyrolysis results, a provisional relation between volatiles and the solid residue in the case of the idealized dispersion test, Figure 3.12 can be resolved for percentage values, as follows:

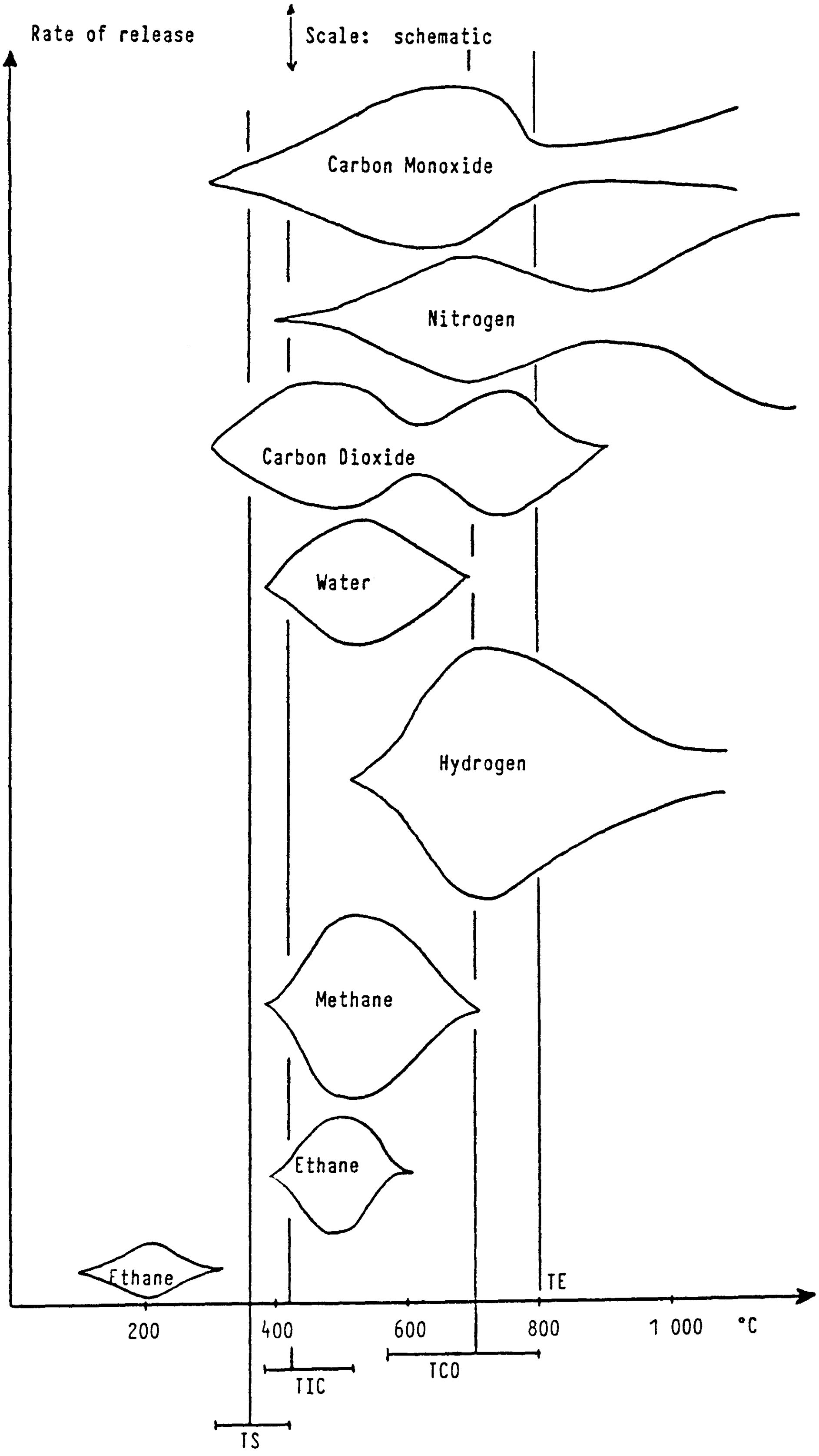


FIGURE 3.14 Volatiles as released (Juntgen 1979) when coal is heated at a slow linear rate

lv = light volatiles originating from broken aliphatic links.
pc = pseudochar, ie dislodged ring complexes, some possibly severed,others possibly still intact and exhibiting poorly developed thermoplastic properties, similar to that of tar. Ash constituents are present, lv released.
fc = char ie a solid with a porous texture and no thermoplastic properties. The texture influences its propensity for burning. High volatiles are released.
ic = graphite or pseudocrystalline graphitoid with a low propensity for burning, probably due to its low porosity. It may form from inert macerals (inertinite) or as a result of carbonisation during burning.
hv = the volatile fraction presumably poor in H_2 which originate mostly from stripping appendices from the ring complexes.

As it is not clear when the final hydrogen is stripped from the aromatic structures, the volatile fraction uv, (E3.0 p 44) was introduced to provide for this element of uncertainty.

According to this conceptual model for dispersion, it is conceivable that FC could represent a dehydrogenated pseudochar, but with a varying percentage of volatiles as rank influences the final temperature of the devolatilization.

3.3.2.3 TG dispersion parameters

The subdivision of the ML curve into dispersion stages seems to be a reflection of the sequence of metamorphic processes which take place when heat is applied to coal. The detail within these stages can be reduced to specific trends, but the particular reactions cannot be identified using TG data only.

Similar coals should be comparable within the stages and thereafter within the lower order stages as outlined. The diagnostic parameters for the substages should be compared rather than comparison of curves by inspection because small variations in form features cannot be identified in this manner.

A complete set of quasi-proximate parameters can be derived from dispersion analysis, but these values need not necessarily correspond to conventionally determined values. The deviations are, however, not excessive and the quasi-proximate values are acceptable as a first approximation, particularly when the ease with which they can be obtained is considered. Table 3.1 shows the variations between TG and assay proximate values on the same samples done during 1986. The standard proximate values determined on coals from the same sources for 1984 are also shown to indicate the natural variations in composition.

From a burning point of view the concepts of volatile matter VM, and fixed carbon FC are difficult to accommodate without further consideration because the value of (cv) depends on the correspondence between vm and VM and, fc and FC.

Although both VM and FC depend on specific experimental specifications, even laboratories using standard techniques can obtain different values. Lowrey (1963, p 208) explains the position and concludes that the term "fixed carbon", as determined, is not an adequate description of the nature of the carbonaceous residue. For the analysis of TG results it is necessary to distinguish the contribution of each carbonaceous phase during burning.

In coal the carbon is mainly present as aromatic clusters connected by aliphatic side chains, especially in vitrinite (Figure 3.13, after Solomon, 1981). However, the structure of other macerals probably deviates considerably from the proposed model. In this regard Stopes (1918, p 22) described fusain (or fusinite) as carbonised wood. This could perhaps be partly related to the small fraction (ic) demarcated by TCO and Te (Figure 3.12). Other macerals of the inertinite maceral group probably have molecular structures intermediate between those of vitrinite and fusinite, and the more inert members may also form part of the difficultly burnt carbon (ic). During the carbonisation second order stage of burning (3A) devolatilised macerals may become carbonised to char and may eventually even be partly graphitised which would also adversely affect their propensity for burning.

TABLE 3.1*

PROXIMATE AND ULTIMATE ANALYSIS VALUES
FURNISHED BY NICR ANALYTIC LABORATORY

		Air dry					Dry ash free				
S. #	@	CV	Mo	As	Vm	Fc	FC	C	H	N+S	O
1	84	18,5	6,3	30,5	21,3	41,9	66,2	77,4	4,07	2,3	16,1
	TG	21,6	4,6	29,6	23,0	42,8	65,0	82,7	4,50	2,5	10,0
	86	20,3	5,1	27,2	22,6	45,1	66,6	77,4	4,24	3,2	15,1
2	84	27,5	2,9	14,1	22,3	60,7	73,1	84,2	4,32	2,7	8,7
	TG	26,3	2,9	17,1	19,6	60,4	75,5	84,2	4,40	2,6	8,6
	86	26,3	3,0	17,1	20,6	59,3	74,2	84,3	3,98	2,9	8,8
3	84	19,8	5,5	31,2	19,9	43,4	68,5	81,7	4,53	2,5	11,2
	TG	22,8	6,9	23,8	20,7	48,6	70,1	83,5	4,50	2,6	9,2
	86	21,1	6,9	24,1	22,8	46,2	66,9	78,9	4,39	4,4	12,4
4	84	24,0	4,3	17,9	27,1	50,7	64,4	80,1	4,63	2,5	12,7
	TG	25,8	3,8	17,6	23,8	54,8	69,7	83,3	4,50	2,6	9,4
	86	25,0	4,0	18,5	27,0	50,5	65,1	80,2	4,70	3,4	11,6
5	84	27,6	2,4	15,3	26,9	55,4	68,1	83,4	4,50	2,6	8,8
	TG	27,6	2,7	13,3	30,0	54,0	64,2	82,7	4,50	2,5	10,0
	86	28,6	2,5	13,4	29,1	55,0	65,3	83,3	5,16	2,7	8,8
6	84	29,2	2,5	11,1	33,0	53,4	63,4	82,9	5,51	2,5	9,1
	TG	28,1	2,7	11,7	26,7	58,9	68,7	83,1	4,50	2,6	9,7
	86	29,1	2,7	11,8	30,3	55,2	64,5	82,8	5,29	2,7	9,2
7	84	29,0	2,8	10,7	29,3	57,4	67,2	83,6	4,62	2,4	9,4
	TG	28,0	2,8	12,0	26,7	58,5	68,6	83,3	4,50	2,6	9,5
	86	28,3	2,9	12,5	27,3	57,3	67,7	83,4	4,70	2,9	9,0
8	84	27,5	2,6	14,2	25,0	58,1	69,9	84,1	4,49	2,0	9,3
	TG	27,0	2,7	15,2	25,2	56,9	69,3	83,4	4,50	2,6	9,3
	86	27,3	2,5	15,3	24,4	57,8	70,3	82,9	4,49	2,6	10,0
9	84	28,8	2,6	12,1	30,0	55,3	64,8	81,9	5,18	2,9	10,1
	TG	26,3	2,7	17,3	23,9	56,1	70,1	83,5	4,50	2,6	9,3
	86	26,7	3,0	16,8	28,2	52,0	64,8	82,4	4,95	3,3	9,4
10	84	22,7	4,0	24,3	27,2	44,5	62,0	77,5	5,28	2,0	14,2
	TG	23,2	3,3	26,1	21,1	49,5	70,1	83,5	4,50	2,6	9,3
	86	22,3	3,6	26,3	25,4	44,7	63,7	79,7	4,91	4,5	10,8
11	84	27.3	3,0	16,1	25,5	55,4	69,0	82,9	5,08	3,0	9,0
	TG	27,4	2,9	13,7	21,0	62,4	74,8	84,1	4,40	2,6	8,7
	86	28,3	2,8	14,0	27,2	56,0	67,3	83,6	4,88	3,6	7,9
12	84	26,4	2,6	19,8	21.9	55,7	70,1	83,8	4,96	2.9	8,3
	TG	25.9	2,5	18,8	22,0	56,7	72,0	83,8	4,40	2,6	9,0
	86	26.7	2,1	19,2	27,2	51,5	65,4	82,5	4,99	4,3	8,3

* Explanation of symbols on next page

TABLE 3.1* (continued)

		Air dry					Dry ash free				
S. #	@	CV	Mo	As	Vm	Fc	FC	C	H	N+S	O
13	84	28,8	3,5	10,3	34,5	51,7	59,9	80,8	5,37	2,2	11,6
	TG	28,2	3,8	10,5	34,5	51,2	59,7	82,2	4,60	2,5	10,5
	86	29,1	3,2	9,9	35,0	51,9	59,7	81,9	5,40	2,5	10,2
14	84	28,1	2,0	15,0	28,3	54,7	67,3	83,7	4,98	2,6	8,7
	TG	28,6	2,6	10,4	27,8	59,2	68,0	83,2	4,50	2,6	9,5
	86	29,9	2,4	10,4	28,8	58,4	66,9	84,1	4,91	2,9	8,1
16	84	30,2	1,5	13,4	26,7	58,4	68,6	87,9	4,82	2,8	4,5
	TG	28,6	1,9	11,2	31,4	55,5	63,8	82,7	4,60	2,5	10,0
	86	31,3	1,5	11,4	28,7	58,4	67,0	87,1	5,19	3,9	3,8
15	84	30,1	1,7	12,1	8,7	77,5	89,2	89,9	3,56	3,2	3,3
	TG	29,6	1,6	12,1	7,5	78,8	91,3	89,8	3,30	3,1	3,5
	86	29,9	1,7	13,6	10,6	74,1	87,4	90,2	3,54	3,6	2,6
17	84	31,2	1,3	12,3	20,7	65,7	76,0	87,9	4,82	2,8	4,5
	TG	26,8	0,9	17,6	23,4	58,1	71,2	83,6	4,40	2,6	9,1
	86	29,0	1,3	17,5	18,5	62,7	77,2	88,4	4,75	2,7	4,2
18	84	30,6	1,7	11,5	10,1	76,7	84,6	90,2	3,74	2,9	3,1
	TG	30,2	1,7	10,3	7,3	80,7	91,7	91,7	3,30	3,1	3,4
	86	31,0	1,6	11,4	11,3	75,7	87,0	90,6	3,83	3,3	2,3
19	84	32,1	1,3	8,6	10,0	80,1	88,9	89,6	3,63	2,7	4,1
	TG	29,4	1,8	12,9	8,3	77,0	90,2	89,9	3,40	3,0	3,5
	86	30,5	1,7	12,8	10,1	75,4	88,1	90,6	3,89	3,6	1,9
20	84	31,0	1,6	10,3	8,8	79,3	89,2	88,9	3,80	4,0	3,4
	TG	29,6	1,5	11,9	7,0	79,6	91,9	89,8	3,30	3,2	3,5
	86	30,0	1,6	12,3	6,4	79,7	92,5	90,0	3,25	5,2	2,1
21	84	29,6	1,9	13,8	8,0	76,3	91,0	90,2	3,33	3,7	2,7
	TG	28,7	2,1	14,5	7,6	75,8	90,8	89,9	3,40	3,0	3,4
	86	29,5	1,9	14,3	7,4	76,4	91,1	90,8	3,39	4,5	1,5
22	84	30,3	2,5	10,3	4,6	82,6	94,7	91,6	2,78	3,1	2,5
	TG	29,3	2,1	12,3	6,4	78,9	92,4	90,0	3,30	3,2	3,3
	86	30,0	2,3	11,6	4,9	81,2	94,3	91,6	2,64	3,3	2,4

S. # = Sample reference number
@ = Origin of data: 84 = published values NICR Bulletin No 98 of 1984
TG = proximate data from TG analysis 1986: ultimate values refer Snyman 1983. (p15 & p18)
86 = assay values of samples 1986
CV = calorific value
Fc = fixed carbon %
H = hydrogen %
Mo = moisture %
As = ash %
FC = Fixed carbon (daf)
N+S = Nitrogen + sulphur %
Vm = volatile matter %
C = Total carbon %
O = Oxygen %

A similar, difficultly burnable residue is also mentioned by Sarkari (1982, p 676): "Carbon and hydrogen in coal are just the same as in any fuel, chemically and physically active or less active, except the type Conardson carbon, which fortunately occurs in too small a quantity in coal". In practice this inert carbon could probably be related to the carbon in fly ash of power stations.

The term "char" from a TG point of view needs clarification: In a standard laboratory analysis, "char", represents "fixed carbon plus ash", being the carbonaceous residue resulting from the heating of coal in a closed container at 850°C, for five minutes. For TG purposes the term "char", also signifies that the particular coal residue has been structurally altered during devolatilisation. This structural alteration of the char influences its propensity for burning: For this reason, char produced by eg S(1,1,1), S(1,1,2) and S(2,1,2) can exhibit different burning responses although the masses could be the same.

The phase structure of the DTG curve could provide an indication of how the char was produced. Although not developed completely, the series of techniques S(2,1,?), (Figure 3.2 p 21), are intended to provide information in this regard.

Normal proximate analysis only expresses the final mass of the carbonaceous residue (fc) under specified conditions, whereas TG analysis simultaneously also scans variations in state over a certain temperature range. VM represents the mass of volatiles which was released under specified conditions, whereas vm, the TG equivalent, also gives a history of the devolatilisation.

The relationship between extended quasi-parameters and standard proximate analyses is shown schematically by Table 3.2.

It therefore follows that different coals may have the same value for VM, which may even be numerically the same as vm, but the latter in terms of the TG dispersion may comprise various kinds of volatiles released in specific quantities at temperatures and times. These finer differences are diagnostic for a given coal, which is also clearly stated by Solomon, (1981, p 66):

TABLE 3.2*

EXTENDED PROXIMATE ANALYSIS DATA DERIVED FROM TG ANALYSIS

S. #	@	(Air dry)							
		mo (%)			as	vm (%)			fc
		gas		water		lv	ho	iv	
1	86		5,1		27,2		22,6		45,1
	TG		4,6		29,6		23,0		42,8
		3,0		1,6		14,5	6,2	2,3	
2	86		3,0		17,1		20,6		59,3
	TG		2,9		17,1		19,6		60,4
		1,2		1,7		11,1	6,2	2,3	
3	86		6,9		24,1		22,8		46,2
	TG		6,9		23,8		20,7		48,6
		2,3		4,6		12,2	7,3	1,2	
4	86		4,0		18,5		27,0		50,5
	TG		3,8		17,6		23,8		54,8
		1,8		2,0		10,8	11,3	1,7	
5	86		2,5		13,4		29,1		55,0
	TG		2,7		13,3		30,0		54,0
		1,0		1,7		17,0	12,2	0,8	
6	86		2,7		11,8		30,3		55,2
	TG		2,7		11,7		26,7		58,9
		0,7		2,0		13,7	12,7	0,3	
7	86		2,9		12,5		27,3		57,3
	TG		2,8		12,0		29,3		58,5
		1,3		1,5		13,7	12,7	0,3	
8	86		2,5		15,3		24,4		57,8
	TG		2,7		15,2		25,0		56,9
		1,1		1,6		12,2	11,4	1,6	
9	86		3,0		16,8		28,2		52,0
	TG		2,7		17,3		30,0		56,1
		1,0		1,7		10,4	11,8	1,2	
10	86		3,6		26,3		25,4		44,7
	TG		3,3		26,1		21,2		49,5
		1,5		1,8		8,1	11,2	1,8	
11	86		2,8		14,0		27,2		56,0
	TG		2,9		13,7		21,0		62,4
		1,4		1,5		8,0	11,7	1,3	

* Explanation of symbols on next page

TABLE 3.2* (continued)

S. #	@	(Air dry)							
		mo (%)			as	vm (%)			fc
		gas		water		lv	ho	iv	
	86		2,1		19,2		27,2		51,5
12	TG		2,5		18,8		22,0		56,7
		0,9		1,6		9,0	11,7	1,3	
	86		3,2		9,9		35,0		51,9
13	TG		3,8		10,5		34,5		51,2
		1,4		2,4		26,0	8,2	0,3	
	86		2,4		10,4		28,8		58,4
14	TG		2,6		10,4		27,8		59,2
		0,9		1,7		19,3	7,7	0,8	
	86		1,5		11,4		28,7		58,4
16	TG		1,9		11,2		31,4		55,5
		0,7		1,2		18,4	12,1	0,9	
	86		1,7		13,6		10,6		74,1
15	TG		1,6		12,1		7,5		78,8
		0,8		0,8		3,5	3,3	0,7	
	86		1,3		17,5		18,5		62,7
17	TG		0,9		17,6		23,4		58,1
		0,7		0,2		10,4	12,5	0,5	
	86		1,6		11,4		11,3		75,7
18	TG		1,7		10,3		7,3		80,7
		0,7		1,0		3,3	3,7	0,3	
	86		1,7		12,8		10,1		75,4
19	TG		1,8		12,9		8,3		77,0
		0,6		1,2		4,3	4,0	0,0	
	86		1,6		12,3		6,4		79,7
20	TG		1,5		11,9		7,0		79,6
		0,5		1,0		3,0	3,0	1,0	
	86		1,9		14,4		7,4		76,4
21	TG		2,1		14,5		7,6		75,8
		1,0		1,1		3,6	4,0	0,0	
	86		2,3		11,6		4,9		81,2
22	TG		2,1		12,3		6,4		78,9
		1,1		1,0		2,7	3,7	0,0	

S. # = Sample reference number
@ = Source of data:
86 = Assay values 1986
TG = Thermogravimetric analysis 1986
ho = vm - (lv+iv) = heavy volatiles

mo = moisture as = ash
vm = volatile matter = lv+hv+iv (%)
lv = light volatiles hv = high volati
iv = volatiles from inorganic carbonat
fc = fixed carbon

"A striking feature of thermal decomposition which was observed for a variety of coals is that the temperature dependent evolution rate of a particular species is similar for all coals".

3.3.2.4 The ML curve for sugar char and the effects of granularity

A typical mass loss curve for a coarse char derived from granular cane sugar (-18 mesh), is given in Figure 3.15. Sugar cane char resembles a coal which has been devolatilised in the absence of oxygen **but it contains practically no ash.** Its dispersion response can therefore hardly be affected by anything but the granularity of the sample.

Three distinct main stages can be identified on the ML curve. The first two main stages are similar to those of coal. The DTG and temperature graphs define TIC. This leads to a second order stage division of 3A and 3B, the first being oxygen adsorption followed by low level exothermal oxidation, probably while adsorbed gas still remains within the grains of char. This is followed by ignition and normal burn out. The absence of an incineration stage is to be expected because the char is homogeneous and should not behave differently towards the end of burning. What is unexpected is that several phases of burning are reflected by the DTG curve. These phases cannot be justified on the basis of different decomposition reactions of the char.

On account of the chemical homogeneity of the char, it seems likely that the grain size distribution could be responsible for the apparent reaction phases. The smaller grains probably burn out more quickly than the larger ones. It should therefore be noted that grain size must also influence the burning characteristics of coal, apart from real different phases of reaction (Figure 3.10 p 38). Before the phases of the ML curve can be properly interpreted granularity effects must be investigated.

The influence of granularity and size distribution on the nature of the mass loss curve can be visualized by means of the scheme depicted by Figure 3.16.

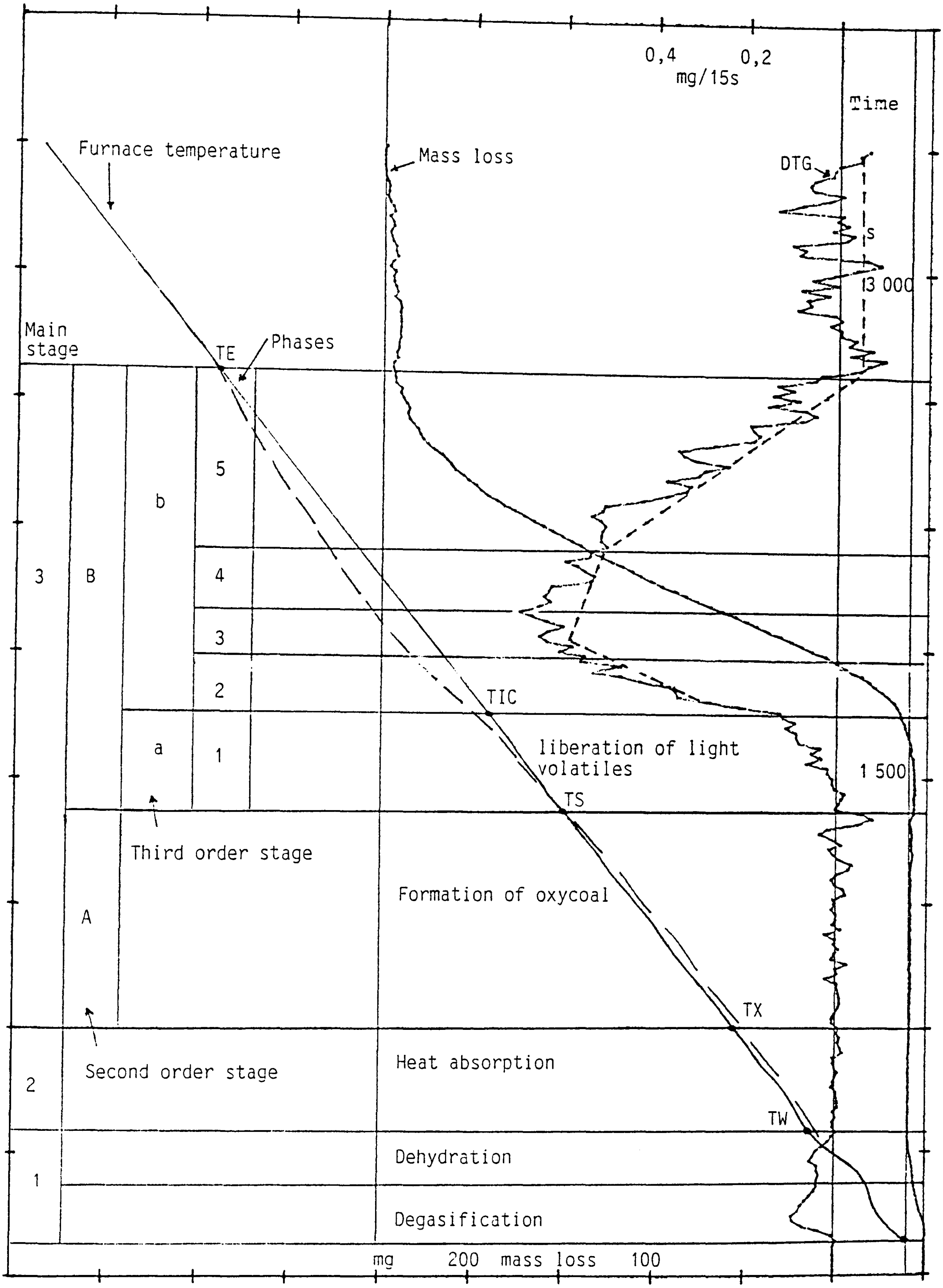


FIGURE 3.15 Possible effect of granularity on a DTG curve

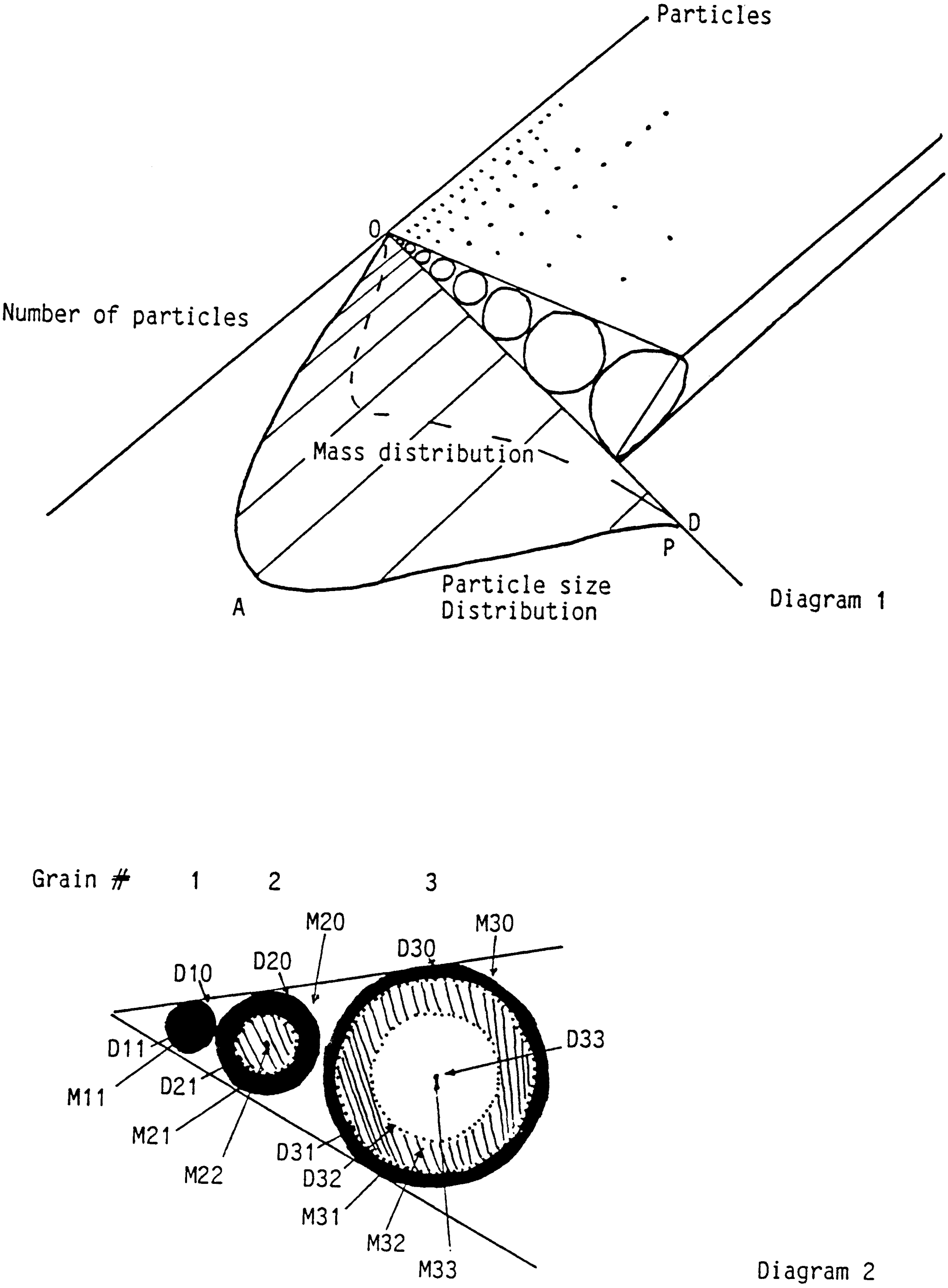


FIGURE 3.16 Progression of a flame front through a burning particle

Diagram 1 shows that the contents of any sample containing a random distribution of different sized grains can be regarded, for purposes of burning analysis, also as consisting of an assembly of particles which are packed in rows according to size as indicated. The hypothetical number of particles envisaged for each row is plotted to show a schematic distribution curve OAP, for the sample. From this data a mass distribution curve can be computed for the assembly of particles in relation to the particle sizes. It should be noted that this flat spread, as far as burn out is concerned is a fair approximation for pulverized fuel, (PF) burning. The burn out of particles which are distributed as a group in space should not be much different from that of a single layer of particles which are suspended as a layer of grains through which air is passed.

If it is assured that all particles ignite at the same instant, the progress of burning can be visualized as depicted by Diagram 2. The equivalent mass fractions which are burnt away, for the times the successive smallest particles burn out, is shown by different symbols and designated as M11, M21, and M31 for the three selected grains. The mass fraction lost during the burn out time for the core of the second smallest particle M22, will be M32 and so on for the complete range of sizes which is present.

The total mass disposed of for the burn out time of eg particle #1 will be M11+M21+M31+.... and likewise, for the other burn out times tb, the appropriate mass lost can be computed. This provides a basis for computing how different particle assemblies will effect burn out.

3.4 The Drop Furnace Technique

The dispersion technique is not entirely suitable for studying all aspects of the exothermic oxidation of coal because the light volatiles (lv) are disposed of before ignition occurs; ie a portion of the fuel, which in practice can produce heat that will enhance combustion, is eliminated.

The best conditions to study burning by means of TG applications are realised in the Drop Furnace Technique. The experimental setting is outlined in Figure 3.1b. The reduction and control systems are the same as those shown by Figure 3.1 (p 18), but the mass balance and temperature sensors as well as the air flow are different.

An extremely steep temperature gradient is achieved by sliding the hot furnace from above over the sample which is contained in a **platinum grid weighing pan,** resting on the scale; ie the furnace is actually dropped over the sample. The furnace slides down at a rate of about 100 mm/s. The sample crosses the thermal step at about 100°C, just outside the furnace, to a temperature of 1100 - 1300°C in about 0,1 s; then moves through this heated zone for about 100 mm, before it comes to rest with the thermocouples spaced at, 10 mm and 2 mm, above and below the platinum container (Tt and Tb, and Tu and Tl respectively in Figure 3.1b). A thermal step exposure, of about 10 000°C/s, which is continuously monitored by A(1), is thus attained. This is reasonably close to the exposure conditions in a PF burner.

To ensure that sufficient oxygen is available, the coal is spread in an even layer over a grid area of about 12 cm^2. The air is passed very gently through the platinum grid of 200 mesh on which the coal rests. The coal charge is about 25 mg/cm^2 of the grid. Air, expanded at about 1100°C, is passed through the grid at a flow velocity of about ten cm per second. This is a rough approximation to a lamellar flow situation into a combustion chamber.

With the drop furnace technique the sample is submitted to all the dispersion stages, except dehydration, which has already taken place outside the furnace at a temperature of about 120°C, before it is submitted to the full furnace heat at around 1000-1100°C.

Air is supplied in such a manner that it is not blown forcibly into the sample but nevertheless exchanged sufficiently rapidly to reduce the accumulation of reaction products.

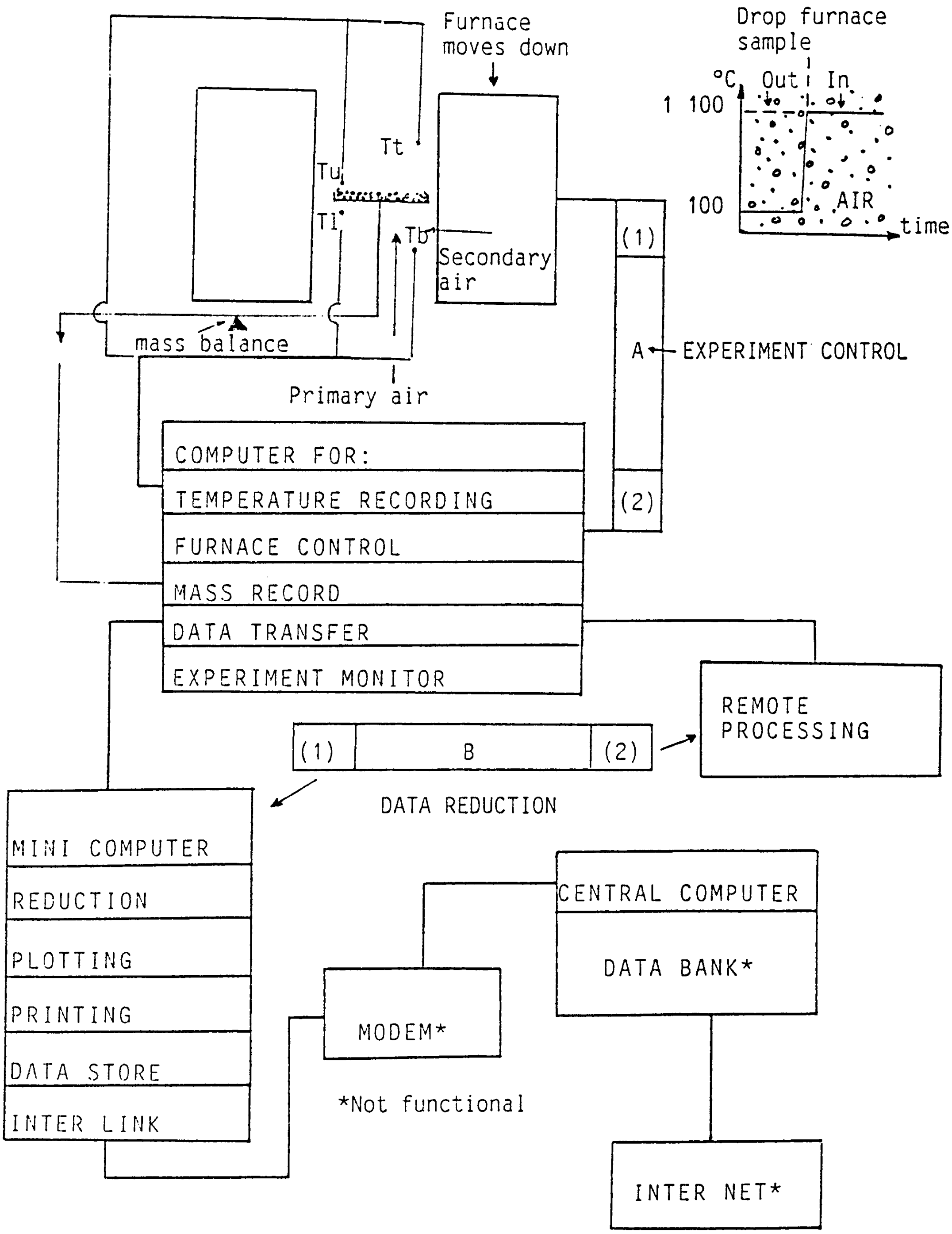


FIGURE 3.1b Drop furnace experimental arrangement

The ensuing mass loss curve will for the sake of distinction, be referred to as a burn out (BO) curve, which is not necessarily a combustion profile. A combustion profile, eg for oxidation of carbon, will be represented by a curve which reflects the rate at which carbon dioxide is generated during the burning process. The burn out curve for eg coal, represents the accumulated effect due to the hypothetical flow, (disappearance ?) of "mass of coal" through a "flame front", from ignition to end. For solid state burning the fuel mass is solid on the one side of the flame front and hot gas on the other side of it.

This distinction is important for TG analysis and is based on the concepts of Zeldovich et al (1985), as used with respect to combustion (op cit, p xviii) and burning (op cit, p 93 and 478). The flame front (op cit, p 92) represents the thin luminous shell, where, due to combustion, the solid fuel is transformed into heated reaction products, by various simultaneous stoichiometric chemical reactions. Movement of the flame front, due to the consumption of the solid, ie integrated mass loss, represents burning, while the reactions occurring within it, constitute combustion. For these reasons, TG measures the result of burning ie a pure mass loss in accordance with a burning law (op cit, p 478). Measurement of the rate of formation of an effluent product, ie combustion, represents an analog to the measurement of the rate of a chemical reaction as prescribed by the law of mass action, and expressed stoichiometrically in a generalized form by E1.1 on page 6.

3.4.1 Physical characteristics of the burn out (BO) curve

The experimental data which can be derived from burn out profiles are shown in Figure 3.17 for sugar char (-70 mesh), and in Figure 3.18 for coal. It can be seen that the proximate percentage values; mo, lv, cc and as, can be determined from the mass fractions depicted in the BO curves. The BO curves are marked as XMIOQ on Figure 3.17 and XMNOP on Figure 3.18.

In the case of char (Figure 3.17) the segment MO is designated by lv. The char was carbonised at 950°C, and is unlikely to yield volatiles other than adsorbed gas, part of which (lv), is

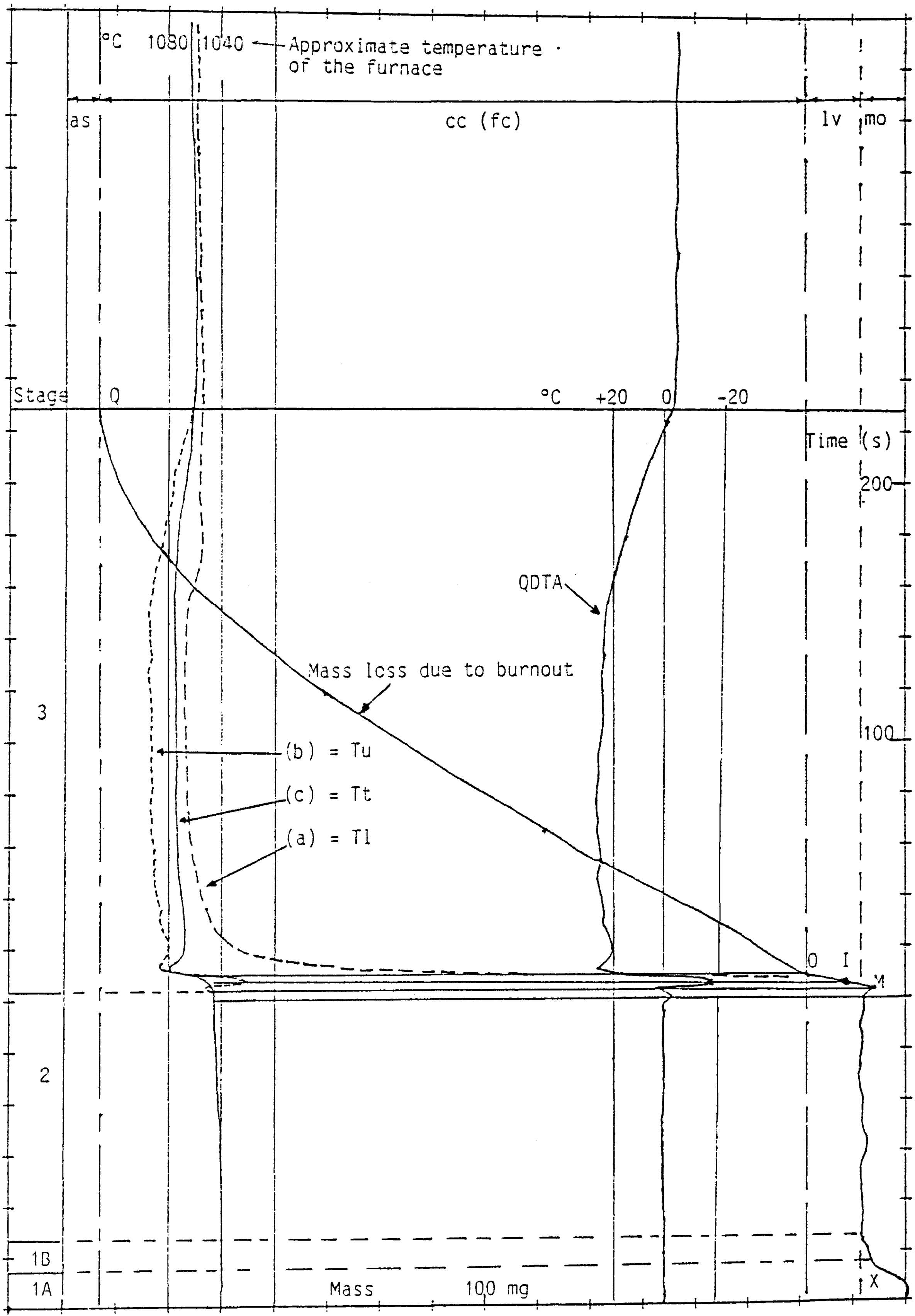


FIGURE 3.17 A drop furnace burnout curve (with temperatures) for sugar char

released on re-heating, ie before ignition occurs. Whether this amount represents the total absorbed gas, cannot be determined from the BO curve, ie using S(3,2,2) in Figure 3.2. When air is excluded by using a closed container, so that ignition is prevented, ie S(3,2,1) in Figure 3.2, the total adsorbed gas, (plus possible volatiles), can be determined using the drop furnace technique.

Sample temperatures are shown by Figures 3.17 and 3.18. Curve (a) shows the rise in temperature recorded by the thermocouple immediately below the sample (Tl), while curves (b) and (c) respectively show the mean temperature of the furnace above the sample (Tt), and in the near vicinity of the sample (Tu). QDTA (given by Tu - Tt) is also shown.

Four stages can be identified in the BO curve for both the char and coal samples. The first point where the system becomes exothermic, ie where the QDTA curve swings upwards (Figure 3.17), is taken as the ignition point of the fuel. Stage 3 represents burning and devolatilization. The first stage represents dehydration but stage 2 has no significance.

3.4.2 The first differential (DBO) of the burn out curve

Figure 3.18 shows the BO and DBO curves for a drop furnace test on coal. It is clear that the DBO curve consists, as a first approximation, of two oppositely sloping straight lines (ab and bc), then a constant value (cd), and a negatively sloping straight line, (de). This means that the section MN of the burn out curve is a section of a positive parabolic function which is intersected by another parabola with downward facing concavity (NO). A straight line segment (OR) follows, and finally again a negative parabolic function (RP). This is an alternative approach to identify stages of burning. In Figure 3.17 temperatures were used for this. The DBO is actually more convenient for this purpose because of the ease with which straight line segments can be identified.

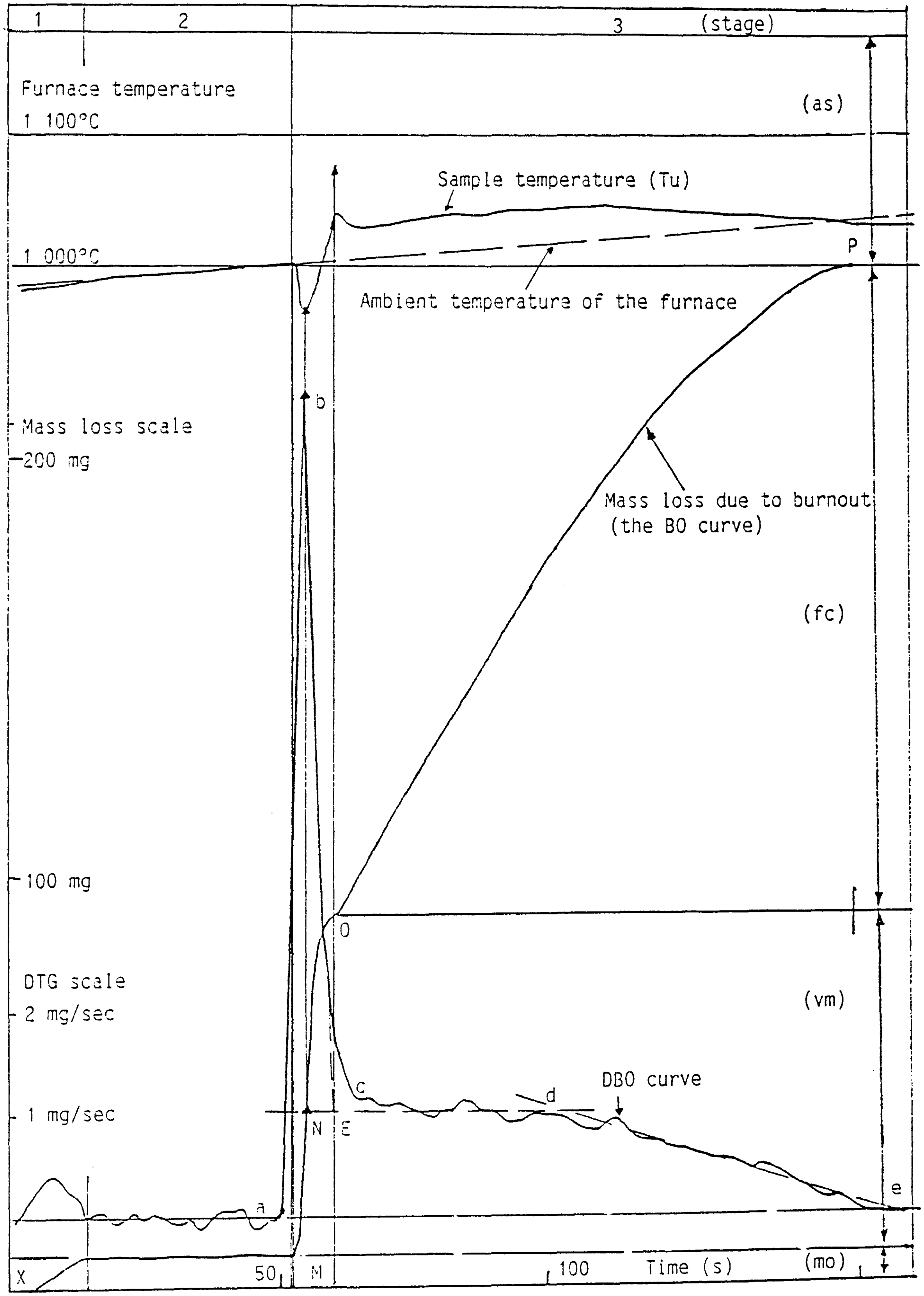


FIGURE 3.18 Results from a drop furnace test on coal

From the considerations above it follows that, like for dispersion, controlled burning of the solid fuel also provides quasi-proximate analysis data. Concerning the stages which can be identified, it should be noted that for dispersion analysis (S(1,1,2), Figure 3.2 p 21) the stages result from a fixed procedure. For the drop furnace (S(3,1,2), Figure 3.2) however, stages 1, and 2, are consequences of operational procedures which can be manipulated at will; eg the time span of stage 2 (dehydration), has no significance, because it is an arbitrary period during which the sample is kept at about 150°C, about 2.5 cm away from the furnace entrance. In contrast fc is a definite significant parameter which is determined by the reaction which applies. It is possible to conduct the drop furnace test without demoisturising the fuel, but dehydration is applied because preheated fuel is generally used in PF burners.

3.4.3 A mathematical analysis of the BO and DBO curves

From an analytical point of view the results of a drop furnace test incorporate all the stages which follow TS, in a dispersion analysis. In Figure 3.19, which represents the same data as Figure 3.17, but with the accent on different features, M represents the starting point on the BO curve XMOPQ.

In the BO curve, two straight line segments (MO and OP) can be identified. By inspection the rest of the curve (PQ) can be surmised to represent a parabolic function of the form,

$$m_2 = A.t - D.t^2 = m_3 - m_4 \qquad E3.1$$

The other two straight segments can be represented as mass loss functions of the form,

$$m_1 = a.t \qquad E3.2$$

and $m_5 = B.t$ E3.3

It follows that the derivative functions for the equations E3.1 to E3.3 will be: $dm_2/dt = A - 2.D.t$, $dm_1/dt = a$, and $dm_5/dt = B$, respectively.

These derivative functions are shown schematically, in idealized form as the DBO curve abcdef, representing the various symbolic

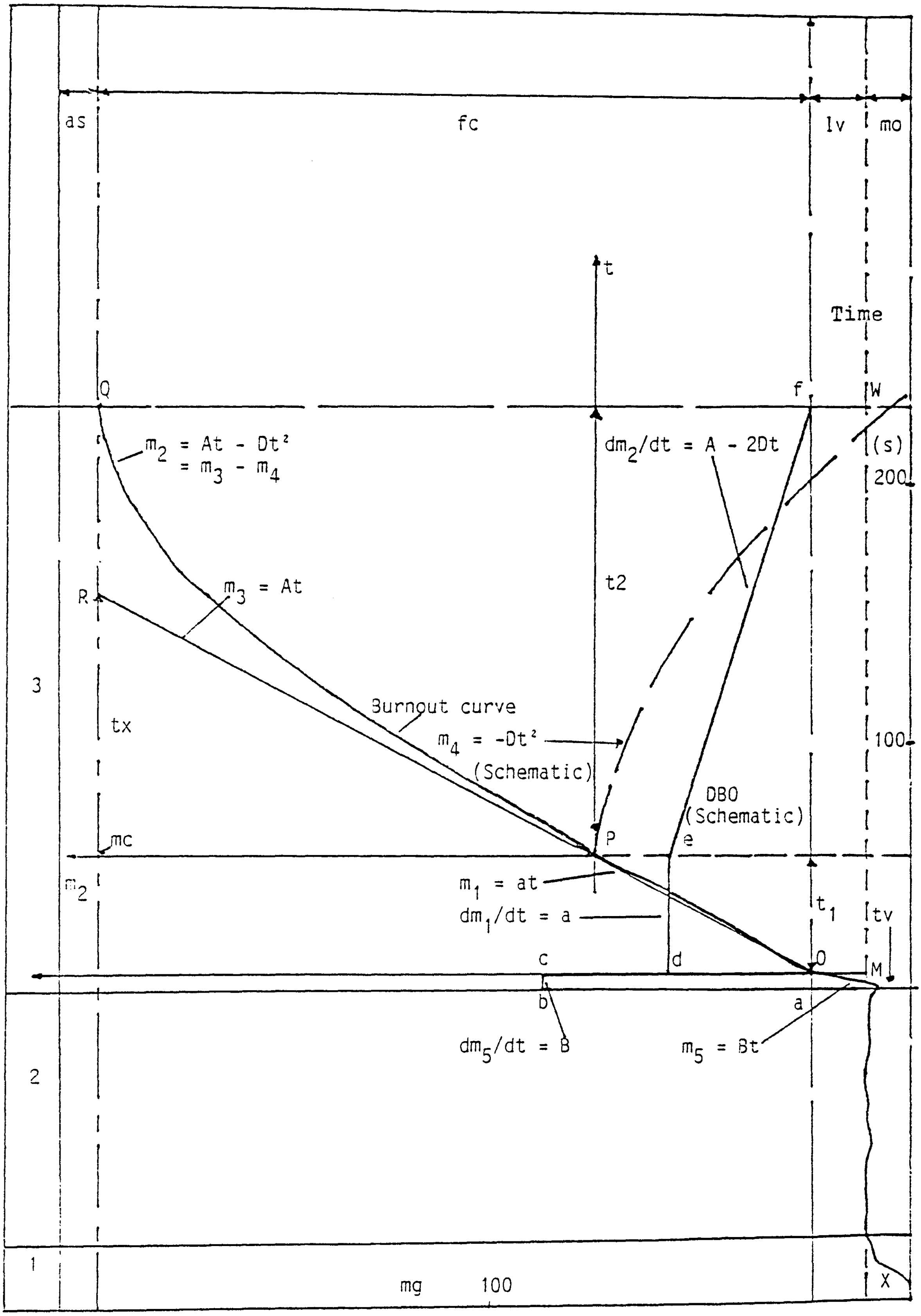


FIGURE 3.19 Analysis of a char burnout curve

functions, eg dm_2/dt, in conjunction with the corresponding BO segments eg m_2
E3.1 consists of two scalar quantities, m_3 and m_4, which functionally represent a linearly increasing, and a parabolic decreasing regression of accumulative mass variation as ordinate, and time as abscissa.

The coefficient A represents the slope of the tangent through the origin of a related axis at P. The related linear function m_3 = At is shown as the line PR and it follows that if the mass release, at a time (tv + t1), continues at the slope rate A mg/unit time, all the residual mass of a start quantity of mc, will be burned out at the time tx, as shown in Figure 3.19.

The observed burn out curve PQ, however, shows that the mass takes a much longer time, ie t_2 to burn out as a result of a "damping" effect D, which is superimposed on the generating function m_3. The damping function m_4 is represented by the parabolic curve PW. The coefficient A can thus be regarded as an "activation" factor which drives the burning reaction. After a certain lapse of burning time, t_1, the mass change (curve PQ) is the result of a linear driving function and a parabolic damping function. The coefficients A and D are not independent of each other; their values only depend on two parameters viz. the mass available for burning at P ie mc, and the time for actual burn out t_2.

The relation between A and D follows from the consideration that, at time t_2, the value of m_2 in E3.1 becomes mc, (Figure 3.19). At time $t = 2.t_2$, $m_2 = 0$ ie $A = 2.D.t_2$. By solving E3.1 for these conditions simultaneously, it follows that $A = 2.mc/t_2$ and $D = mc/(t_2^2)$. A and D are therefore not independent parameters: $D = A/2t_2$.

In the segment OP of the burn out curve, (Figure 3.19), the linear function E3.2 shows that burning proceeds in a linear fashion without any damping. The activation coefficient a, can be derived from the slope of the line OPR with the origin at O. Similarly the first response, ie degassing, is represented by line segment MO and the release rate B, also follows from the slope of the line. Both these latter functions are solutions of

E1.1 for $n = 0$ ie the reactions are of zero order. As burning progresses the rate constant (a) becomes affected by damping which slows down the reaction. This damping cannot be due to the effect of the presence of ash because the fuel is almost pure carbon. The damping effect, which is generated by the rate of burning itself, can only be ascribed to the effect of depletion of oxygen in conjunction with the formation of reaction products and/or the distribution of the grain sizes: It is most likely that transport phenomena are a disturbing factor.

Figure 3.20, for the same data as in Figure 3.18, shows how the BO curve can be expressed mathematically by identifying approximated linear functions comprising the DBO curve. The only really significant difference between the drop furnace data for char and coal (Figures 3.19 and 3.20), is in the release of the volatiles and the length of the undisturbed progress of the zero order reaction. In order to keep the equations simple, the time origin is shifted in succession from M to O to P. The burn out process is regarded as consisting of three discrete operations where m_5 represents mass of volatiles, m_1 mass of pseudochar and m_2 mass of char with time t_1 as common variable. The burn out times for volatiles is tv, that for pseudochar t_1, and for char t_2.

The important information revealed by these two kinds of burning profiles is:

a. Drop furnace tests show that the multiple processes revealed by dispersion tests can fundamentally be simplified to two dominant ones namely (i) release of volatile matter, which is ignited and burns to produce virtually instant heat, and (ii) a much slower process described as burn out, of the char. This burn out occurs in two stages. Firstly char with some residual volatiles burn linearly and finally the char depleted of volatiles burns out in a damped fashion.

b. From the mathematical analysis of the empirical TG data, burning activation and damping functions can be derived. These functions can be used to estimate the **unique burning behaviour** of a given coal when the coefficients are known.

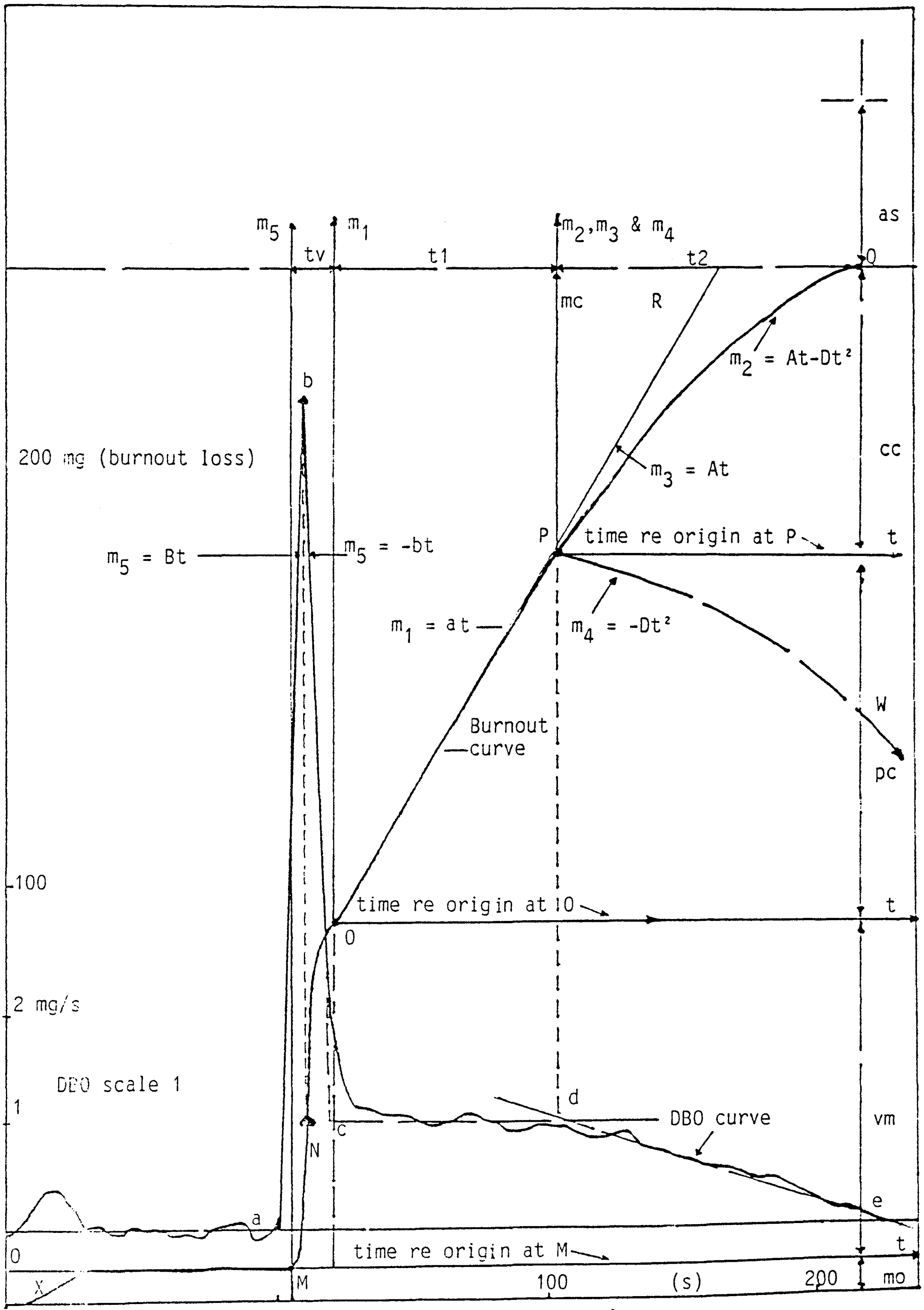


FIGURE 3.20 Analysis of drop furnace burnout for coal

c. An important factor which, however, is not known is the relation between the TG determined analytic parameters such as A and D, and the standard chemical kinetic parameters eg k and E, which are commonly used for delineating the stoichiometric chemical mechanisms for the oxidation reaction of fuels at high temperatures, namely combustion (k = rate constant and E = activation energy).

3.4.4 An empirical approach to burning parameters

It is evident that both the volatiles and the char are burned in the presence of each other in the drop furnace test. The process is compounded so that for practical analysis three major reaction categories can be identified viz. burn out of (i) light volatiles, (inflammability) (ii) high volatiles (conflagration) and (iii) char (glow burning) (Figure 3.20). The drop furnace, as a natural process of integration therefore only reveals the ultimately predominant responses of fuel to heat. The dispersion technique on the other hand serves to reveal information regarding the detailed response to small increments of heat, thereby revealing the components which comprise burning of different coals.

Since the burn out curve as obtained from a drop furnace test reflects an acceptable emulation of real solid fuel burning, it will be analysed in terms of Essenhigh's exposition, of the **"two-component hypothesis"** for the thermal decomposition of coal. Essenhigh (1955), put forward the hypothesis that coal could be dissociated into two components by gentle heating viz (1) a volatile component which was easily evolved (and may be denoted by Ve) leaving (2) a solid residue which, by the application of intense heat, could itself be dissociated into the volatile residue (Vr) and fixed carbon (Cf).

According to this view the basis for the S(1,1,2) and S(3,1,2) techniques Figure 3.2, which discriminates between dispersed and compounded responses, is well founded. The easily evolved volatiles Ve can be regarded as equivalent to light volatiles (lv) and Vr to heavy volatiles (ho). From this relation it follows that for the analysis of coal decomposition under oxidizing conditions, the following factors are of importance:

a. The relative smoothness of the burn out curve, ie in terms of reaction phases as reflected by the DTG of a dispersion process, indicates that combustion and other reactions of the fuel components overlap to such an extent that the appearance of a relatively homogeneous process is created when burning is used as a basis for measurement. The DTG curve in Figure 3.11 derived from the ML curve shows how erratic burning can be. The effect of the distribution of grain sizes appears to be evened out to some extent when volatiles and char burn together.

b. Analytical procedures as applied for homogeneous reactions with the view of deriving unique chemical parameters must be misleading as it is not possible to determine the real cause of a deviation which is measured. The resultant of too many processes is measured as a single scalar parameter, mass.

c. The predominant features of the observed data expressed as continuous functions must be used as a basis for interpretation. The features most likely to be diagnostic in connection with assessment of the burning properties of coal appear to be linked with the nature of the three components as outlined by Essenhigh. The manner in which volatile matter is released **and its composition** as well as the burn out pattern of the carbon appear to dominate the process of burning. It is not necessarily the quantity (vm) which controls effective burn out but the quality.

d. Production of heat through burning of coal must derive from the two volatile components, lv and ho, which can be combined as volatile matter vm and the carbon which is not contained in the volatiles ie fixed carbon fc. For coals from a specific locality, or even a region, it can be expected that the composition of the volatiles should not vary unduly as a result of the laws of sedimentation. The heat content of the volatiles can therefore be determined as a constant which forms a component of the calorific value of the coal. Since carbon is a pure element it has a definite heat value associated with it. If the calorific value of the volatiles is denoted by KV and that for carbon HC, then the calorific value for coal CV, can be expressed as CV = KV + HC.

The CV of char with different ash contents was determined on several different samples and an average value of 32,9 MJ/kg was established as an acceptable mean value: Grimsehl (1933, p 147), provides a value of 33.06 MJ/kg for graphite and 33.48 MJ/kg for amorphous carbon.

By using this value in conjunction with FC ,VM and CV, for published analysis of all SA coals the relation:

$$KV = (100.CV - FC.32,9)/VM,$$

expresses a calorific value KV (in MJ/kg) for the volatile matter (vm) of coal.

Knowing KV and HC the formula,

$$cv = [(KV \;.\; vm) + (HC \;.\; fc)]/100 \quad \text{MJ/kg (coal)}$$

can be used to compute the calorific value using TG derived parameters.

This procedure ignores the fact that KV also represents non-combustible volatiles iv and mv, and combustible inorganic volatiles me. It follows that if appropriate values of KV are used as constants representing different coals, a good value for cv can be calculated using the TG proximate parameters for similar coals ie cv and fc (Refer Table 3.1 p 56). An overall mean value of KV = 33,04 MJ/kg was determined from computations using many coal analyses published annually by the National Institute for Coal Research. Separate group values were also determined for coals from different areas and also for anthracites.

e. Since cv, through the manner in which it is computed, tends to correspond well with CV, knowledge about iv is important in connection with the sustained burning properties of coal. In this regard Essenhigh states, (1955, p 498), "Inflammabilities, however measured, were presumed to be a function of Ve the easy burning volatiles, (or the combustible fraction thereof), and this being largely independent of Vr, the volatile residue, explained the well substantiated result that the correlation between inflammability and Vt, total volatiles, was very poor". It follows that a high iv and mv, ie a poor quality of volatiles, could point towards unsustained burning. (For coal products usually hv = ho applies because the beneficiation process reduces the effects of iv, mc and me.)

3.5 <u>The kinetics of coal reactions during combustion</u>

The chemical reactions which apply within the flame front are governed by the laws of chemistry. It is, however, not clear if the total effect of all the reactions which occur simultaneously and which is recorded as a ML or BO curve, can be analysed using the principles which apply to a single component reaction. If this reaction occurs in the solid state the situation is more difficult. Justification for equating TG mass variation curves with rate of chemical reaction phenomena requires discussion.

Zeldovich <u>et al</u> (1985, p 21) discussed the oxidation of graphite and makes the following statement: "The strong bond of the C atom in solid carbon means that carbon does not vaporize. Carbon leaves the solid state only in combination with oxygen in the form of CO or CO_2 ". This clearly suggests a reaction mechanism of chemisorption and desorption which in turn points to a zero order mechanism.

The results obtained from the BO curve seem to fit this supposition ie the coefficient A, in E3.1 does represent the rate constant. For the case of dispersion and other solid decompositions further consideration is required.

3.5.1 **Activation energy and coal reactions**

The rate of a chemical reaction is firstly governed by the law of mass action Findlay (1943, p 319) and secondly it is related to temperature by the Arrhenius equation (Moore 1957, p 546 & 570)

$k = Z.\exp(-e/T)$ E3.4

k = Rate constant.

e = E/R = E/8,31

R = Gas constant.

E = Activation Energy for a particular mole of a given reaction.

Z = Frequency factor (approx. 10^{13} for unimolecular reactions, Moore, 1957, p 570)
T = Absolute temperature.

E represents the critical energy which a molecule must acquire before it can react. It follows from E3.4 that large values of E imply the presence of relatively few activated molecules and slow reaction rates (Findlay 1943, p 347). E could thus serve as an inverse indicator of relative reactivity when the mole which controls the reaction can be identified.

Since activation depends on the number of molecular collisions which occur (ie Z, in E3.4), it follows that exp(-e/T) represents the fraction of molecules which are in the activated state at a given temperature. From E3.4 follows that:

$$\ln(k) = \ln(Z) - e.(1/T) \qquad \text{E3.5}$$

which is a linear function in (1/T)
with $d[\ln(k)]/d[1/T] = -e = -E/R$

E, can thus be determined from experimental data by determining k for different temperatures and by plotting the results. This graph is referred to as an Arrhenius plot and is used in connection with the Law of Mass Action which specifies k in terms of the rate equation for homogeneous chemical reactions viz.:

$$dm/dt = k.(mc - m)^n \qquad \text{E3.6}$$

mc = Initial concentration of the reactant in moles/liter.
m = Number of moles which have reacted after time t.
n = Order of the reaction
k = Rate constant

If mr = (mc - m) then d(mr)/dt = - dm/dt and,

$$d(mr)/dt = -k.(mr) \qquad \text{E3.7}$$

mr = The amount of reactant which is unreacted after time t.

Solving E3.7 for the case where mr = mc for t = 0 provides the solution:

$$mr = mc \,.\, \exp(-k.t) \qquad \text{E3.8}$$

Solving E3.6 for m = 0 when t = 0 yields the solution:

$$m = mc.[1 - \exp(-k.t)] \qquad \text{E3.9}$$

For E3.8, if $k.t = 5$, then $mr = 0,007.mc$ ie approximately zero for relatively small mc, and similarly, for E3.9, $m = 0,993.mc$, which approximates mc. Let tb represent the time for which $k.tb = 5$ ie tb = the time required for **practical** completion of the reaction: Mathematically the reaction never ends.

If the start concentration mc, (moles/l), for any first order reaction, ie $n = 1$, and tb, is known, the complete history of how m varies during the reaction can be reconstructed through E3.9.

Since $tb = 5.t_1$, and $k_1.t_1 = 1$ for a given experimental setting it follows that $k_1 = 5/tb$ E3.10

Using E3.4, the case for which the rate constants say, k_2 and k_1, are known at two given temperatures T_2 and T_1, where $T_2 > T_1$, can be solved for the activation energy E (Findlay 1943, p 347).

$$E = [\ln(k_2/k_1).R.T_2.T_1]/(T_2 - T_1) \qquad \text{E3.11}$$

For a TG dispersion test the char burn out starts at TIC and ends at TCO: this represents a case where the start rate constant is known. (Refer E3.10)

If a value for k_2, the rate constant at TCO can be found, E3.11 can be solved for the third order burning stage of a dispersion ML curve.

When the activation energy of a heterogeneous reaction is considered it follows that as a result of the many reactions which are involved, several activation energies must apply. In reality thus the expression, "activation energy of coal" has no meaning. Since such an average value is however computed it is designated by the symbol Ea. Moore (1957, p 585), describes Ea as follows: "This Ea is called the **Apparent Activation Energy**, since it is usually a composite quantity, including not only the true activation energy of the surface reaction Et, but also heats of adsorption of reactants and products".

In general using different temperatures of a dispersion analysis, a value for the equivalent of Ea, for what it is worth, can be computed.

Solely for the purpose of determining the order of how Ea for char varies for different dispersion tests which operate within comparable temperature ranges, a value for k_2/k_1 can be derived as follows:

The values for Ea at TIC and Te = TCO for char are determined from the TG data obtained from a TG analysis as shown in Figure 3.25 where TCO and TIC are 720 and 500°C respectively. The value for Ea at TCO = 35 kJ/mole. Using E3.11 it follows that:

$$k_2/k_1 = 3{,}3$$

This changes E3.11 as follows:

$$Ec = \ln(3{,}3).8{,}31.[(TCO+273).(TIC+273)]/(TCO-TIC) \qquad E3.12$$

Ec = Quasi activation energy for the <u>char products</u> of coal:

Particular reference to char follows from the situation that the light volatiles are driven off before TIC is reached; therefore the partly carbonised coal is ignited: At TIC the coal has not been carbonised completely but the complexity of the total combustion process has been reduced appreciably as the result of the disposal of the light volatiles.

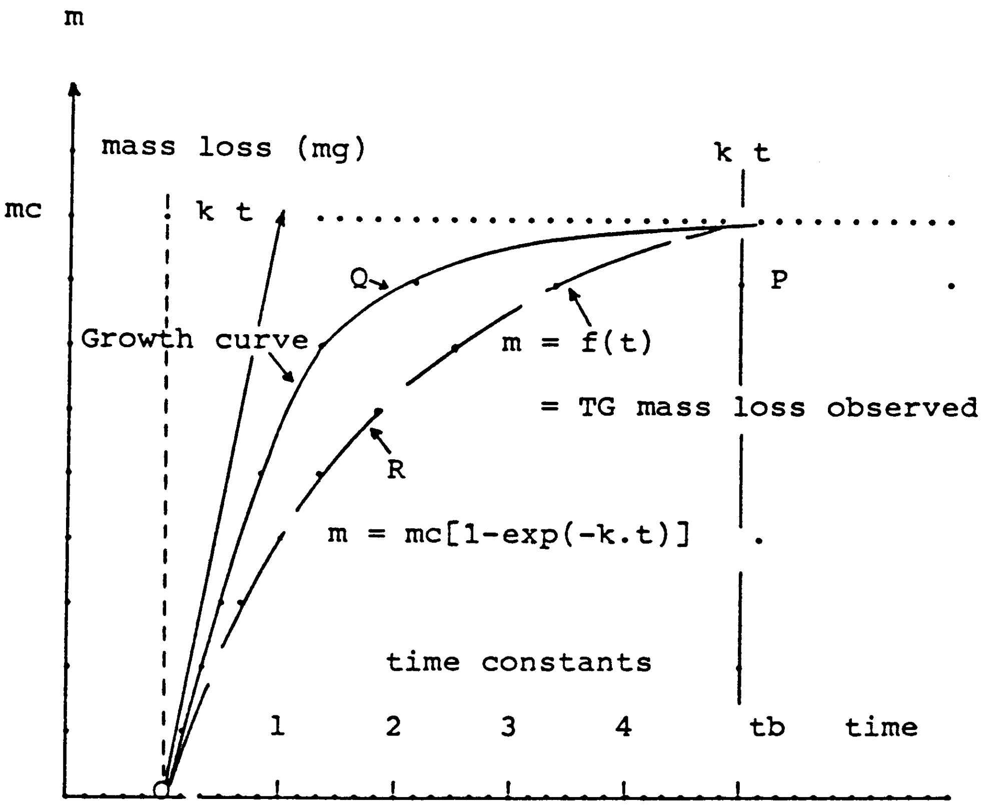
Figure 3.21 illustrates a convenient way in which a TG, ML curve can be tested for first order kinetic features namely **natural growth or decay:**

Let ORP represent the observed mass loss curve from which tb, and mc, can be determined. The value of k follows from E3.10, and substitution into E3.9 yield:

$$m = mc.[1-\exp(-5.t/tb)] \qquad E3.13$$

Solving E3.13 for various values of t, will provide the data for curve OQP which represents the natural growth curve defined by the fundamental parameters mc and tb, for m=f(t). If the observed ML curve ORP coincides with OQP, f(t) is a growth function. This technique is very convenient for a quick test if TG curves conform to a first order reaction or a parabolic response.

Figures 3.22 and 3.23 present the results of testing the observed TG Dispersion and Drop Test mass loss curves for correspondence with exponential and parabolic growth curves. The same data are



<u>FIGURE 3.21</u> Growth test for TG mass loss curve

presented as for Figures 3.17 and 3.18.

Results of the char sample are shown by Figure 3.22. Curve BSP represents the expected exponential growth function of a homogeneous reaction which commenced immediately after the physically adsorbed gas was released. Curve BTP represents the expected parabolic growth function of the form, $m = A.t - D.t^2$ if this function was followed over the entire time of the reaction.

Curves CYP and CXP, respectively represent an exponential and a parabolic function based on the observation that, immediately after the release of the adsorbed gas, the reactions initially proceeded in a distinct linear fashion. This first phase of the reaction would therefore be zero order. The origin for the next phase of the reaction is transferred to C. The second part of the process is reflected by curve CP. The k, A and D, parameters are shown along with the mathematical equations. For both the observed or the indicated two-phase reactions, an exponential, ie first order reaction does not apply because the curves differ too much. The parabolic approach however, is fairly close to what happens in practice and may serve as an empirical expression for the burn out process.

For the case of coal, presented in Figure 3.23, and using the same symbols as in Figure 3.22, it can be seen that the respective curves (BCP) for coal and sugar chars are very similar. A comparison of the coefficients for the best fitting curves, ie BC and CXP for sugar char vs. coal char are presented in Table 3.5.

At the beginning (curve BC) the coal char (Figure 3.23) burns faster (a = 1,07) than sugar char (a = 0,97). This could be due to the absence of volatiles in the sugar char. Towards the end of the burn out process the sugar (pure) char burns faster (A =1,24) than the coal char (A = 1,19). This may be due to the presence of ash in the latter. The damping, ie D coefficients, are very similar probably suggesting similar grain size distributions.

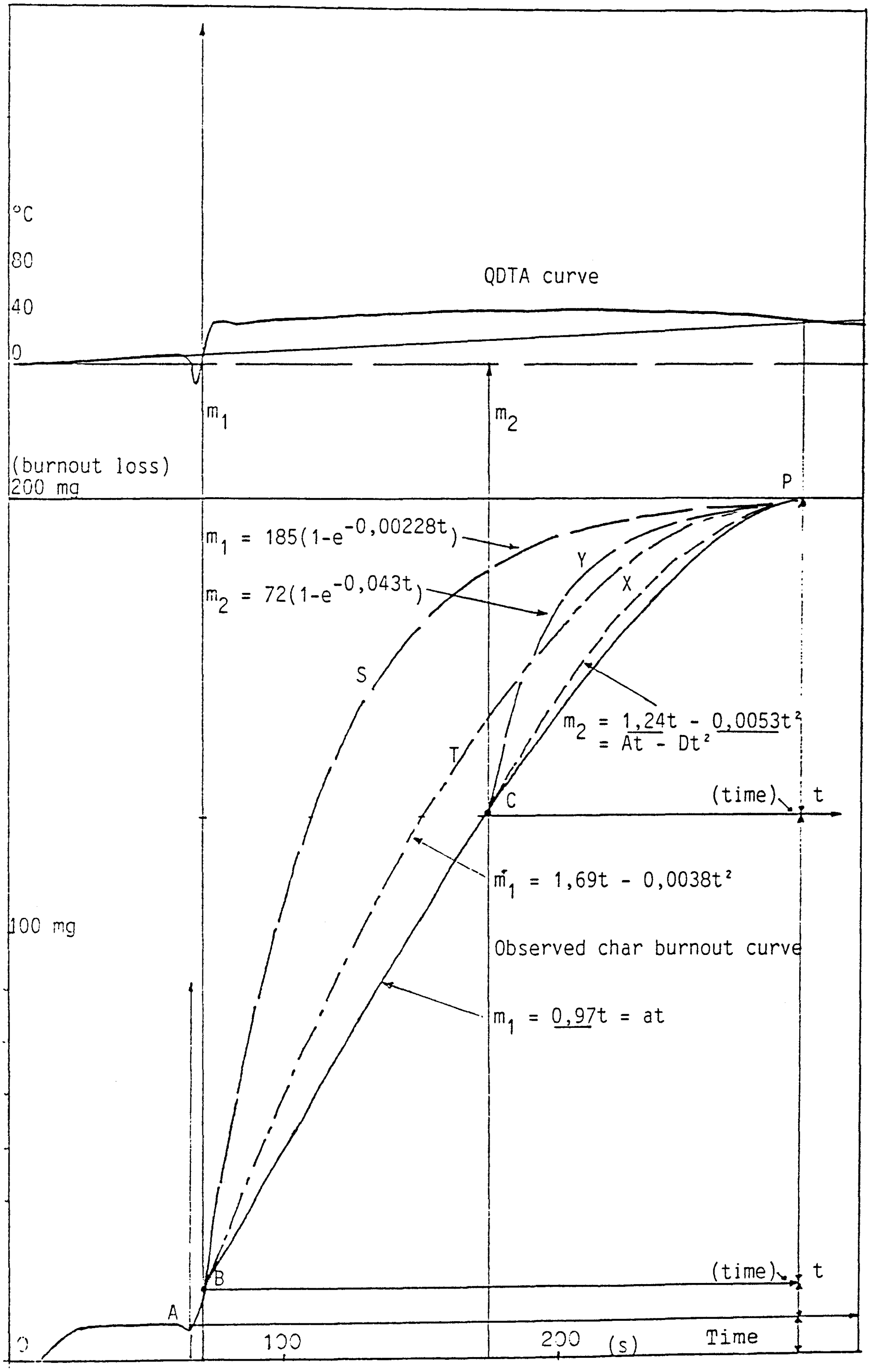


FIGURE 3.22 The burnout vs kinetic parameters for char

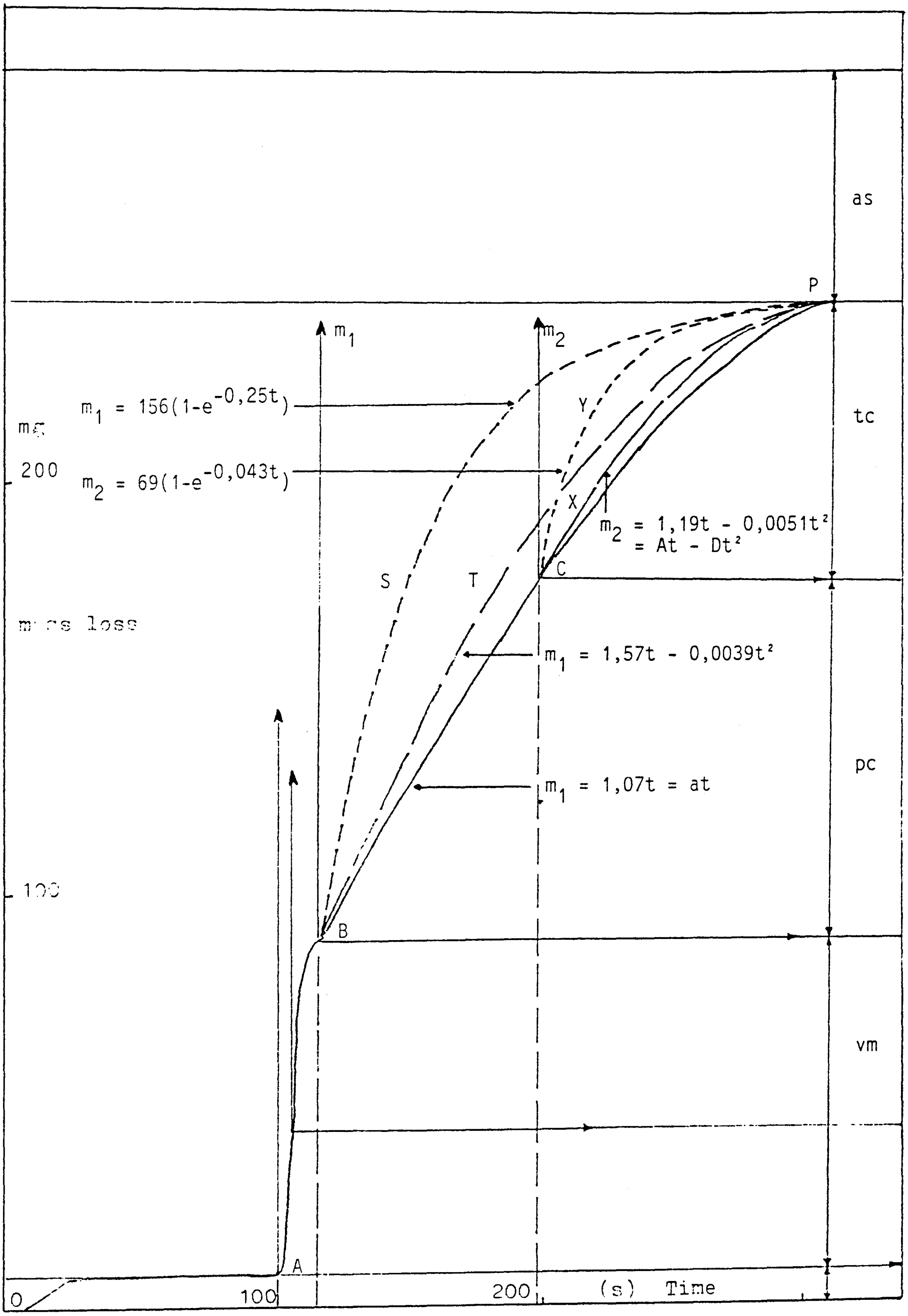


FIGURE 3.23 Char burnout parameters for coal

TABLE 3.5

Comparing burnout coefficients:

$m=a.t$ and $m=A.t - D.t^2$

	Sugar Char	Coal Char	
a	0,97	1,07	mg/s
A	1,24	1,19	mg/s
D	0,0053	0,0051	mg/s^2
	Figure 3.22	Figure 3.23	

a = linear rate coefficient

A = activation coefficient

D = damping coefficient

3.5.2 Kinetic data from coal

Computing kinetic parameters for coal using TG data is fraught with difficulties and the published results vary within wide limits (Table 3.6).

Regarding the activation energy, Unsworth (1986) stated that TGA burning profiles of coals are frequently used by designers and operators of power stations to compare burning characteristics of coals. Kinetic parameters from Arrhenius plots of such profiles, however, cannot readily be related to any specific stage of combustion. From the present analysis it is also clear that dispersion TG has a slim chance of furnishing reliable data regarding the activation energy of coal Ea, ie if such a parameter can be determined.

Especially as a mole of coal cannot be defined, reason for doubt about the usefulness of Ea exists, and Unsworth's statement appears to be justified.

The formula used by (Serageldin <u>et</u> <u>al</u>, 1983, p 12), adapted for natural logarithms, is as follows:

$$(dmr/dt)/mr = \ln(Z) - [(Ea/R).(1/T)] \qquad E3.14$$

mr = mass residue at time t after start of the reaction T=temperature, R = 8.31., dt = time differential.

Let 1/T = C. Differentiation of E3.14 with respect to C will yield a formula for the computation of Ea in terms of the mass changes as expressed by a TG mass variation curve for sugar char, which is a homogeneous compound. No mention is made of molar concentration concerning the coal in the original script Serageldin <u>et</u> <u>al</u> (1983).

$$Ea = 8,31.d[(dmr/dt)/mr]/dC \qquad E3.15$$

Figure 3.24 shows the growth law curves in relation to the ML curve. At points O and P all three curves coincide ie all three functions apply. In terms of temperature, O corresponds with TIC and P with TCO. The value for Ec, computed by using E3.11, is shown in Figure 3.25 along with the continuous variation of Ea, from E3.15, as deduced from the ML curve recorded for sugar char.

TABLE 3.6

Values referred to for activation energies for coals.

Activation energy	Remarks	Reference
20 -40 (kcal/mole)	Anthracite	Essenhigh, 1963, p 187
50 -60 (kcal/mole)	Small part.	Essenhigh, 1970
50 -60 (kcal/mole)	Early value	Essenhigh, 1966, p 18
15 -30 (kcal/mole)	Recent value	Essenhigh, 1966, p 18
200 - 230 (kJ/mole)	British coals	Elder, 1981
200 - 400 (kJ/mole)	Austral.coals	Elder, 1981
198 - 220 (kJ/mole)	American coals	Elder, 1981
25 - 70 (kJ/mole)	Technique 1	Serageldin 1983, p 12
200 -400 (kJ/mole)	Technique 2	Serageldin 1983, p 12
100 -200 (kJ/mole)	Technique 3	Serageldin 1983, p 12
	(Same US coal)	
3 -4 (kcal/mole)	Stage 1	Van Krevelen & Shuyer 1956, p 324
6 (kcal/mole)	Stage 2	Van Krevelen & Shuyer 1956, p 324
16 (kcal/mole)	Stage 3	Van Krevelen & Shuyer 1956, p 324
25 - 35 (kcal/mole)	Stage 4	Van Krevelen & Shuyer 1956, p 324

Stage 1 : Formation of peroxygen

Stage 2 : Decomposition of peroxygen

Stage 3 : Formation of oxycoal

Stage 4 : Combustion

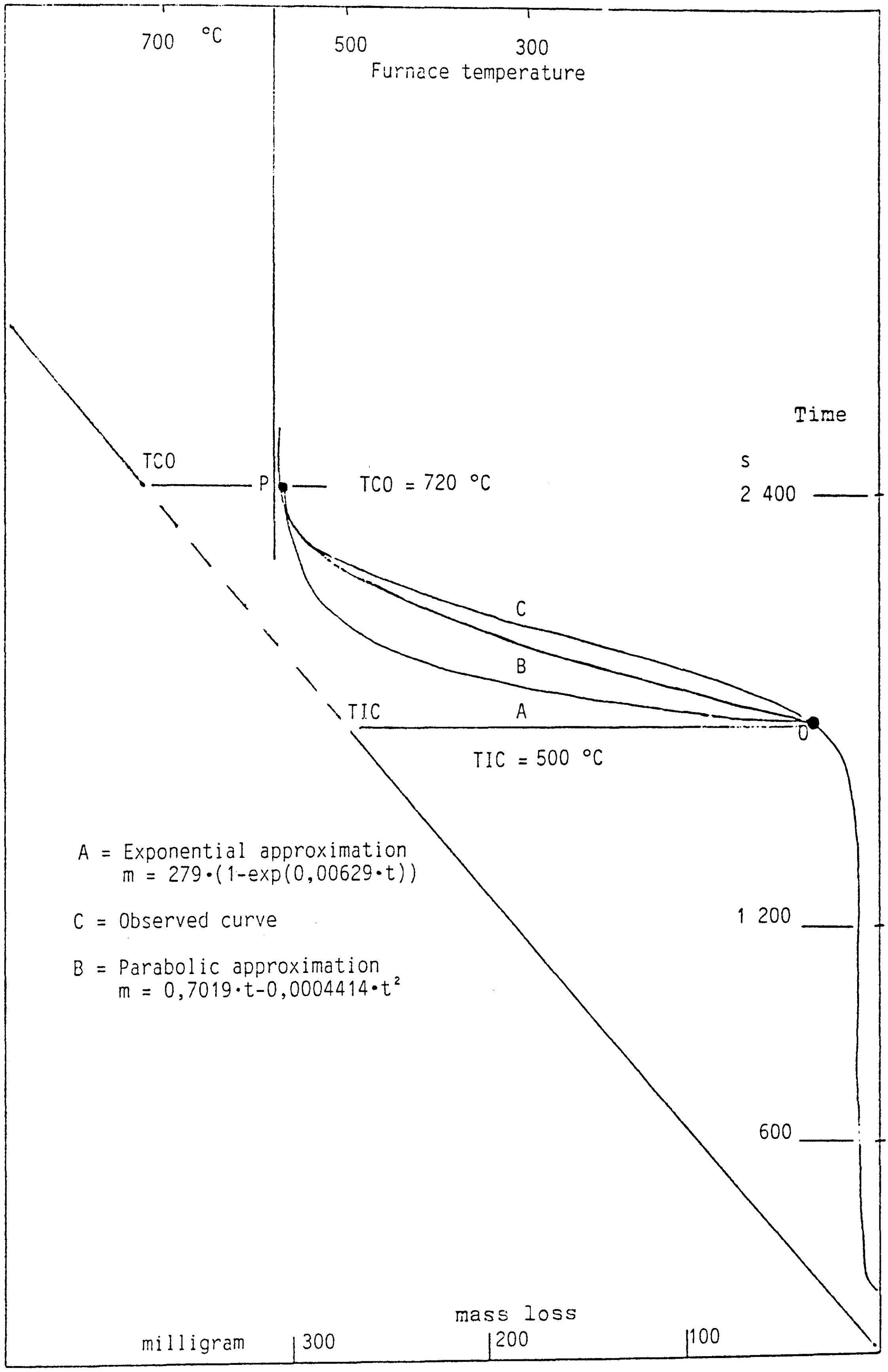


FIGURE 3.24 Kinetic and burnout functions for a char dispersion curve

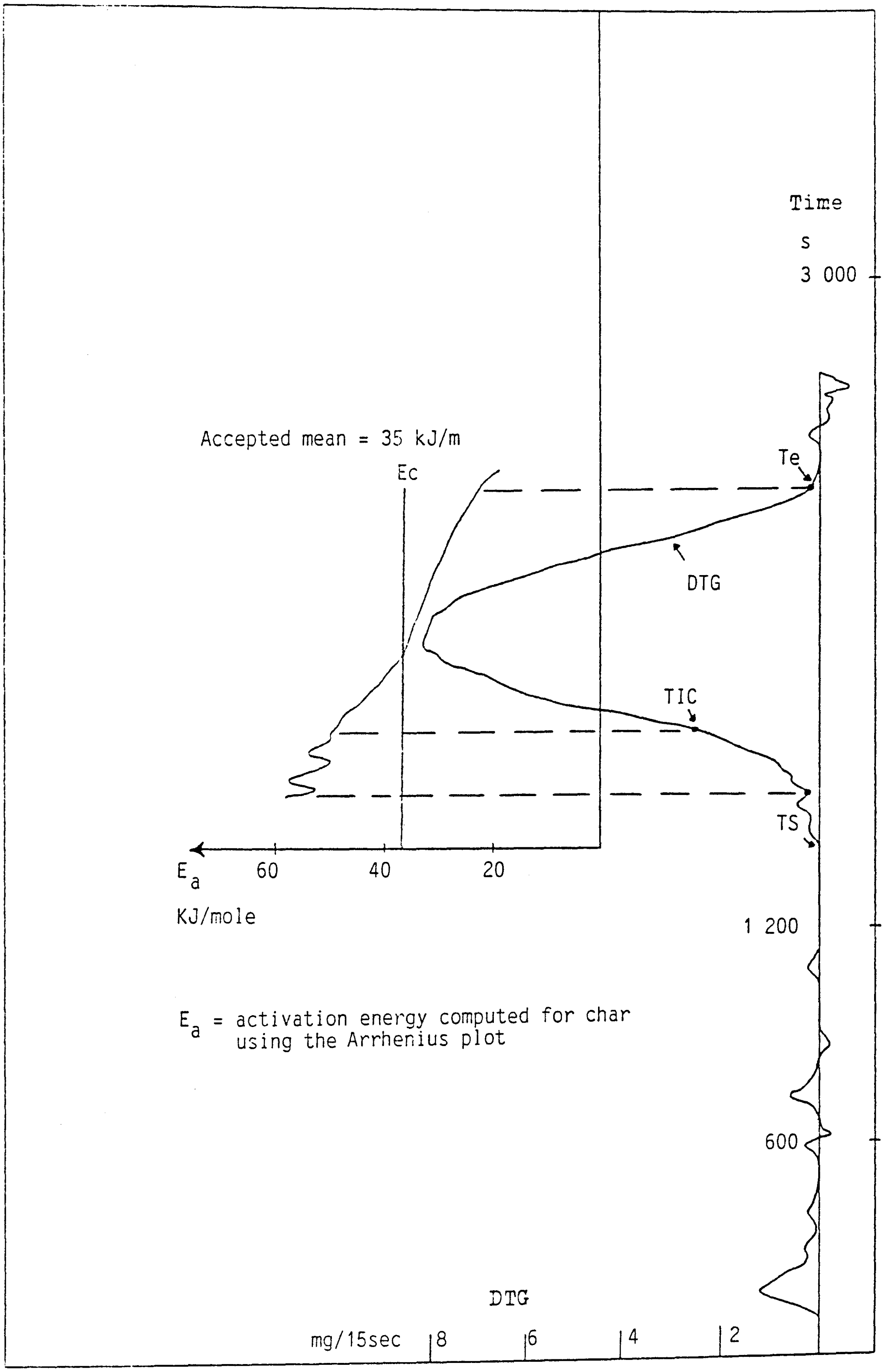


FIGURE 3.25 Activation energy values for char

It can be seen that Ea in air varies between about 58 and 20 kJ/mole of carbon. Char, in terms of Ea as an index for reactivity, becomes progressively more reactive after ignition as shown by the slope of the Ea curve.

The observed ML curve therefore in general does not fit a first order mechanism when either coal or char is used (Figures 3.22 ,3.23 and 3.24).

In view of the problems associated with the application of TG to solid reactants and with the stochastic behaviour of coal, it was decided to investigate the behaviour of model compounds during TGA in order to eliminate some of the uncertainties. It was hoped to obtain indirect indications concerning the thermal behaviour of coal.

3.5.3 Diagnostic features of thermal reactions in model compounds

Since the TG method can only respond to reactions which cause a change in mass in relation to temperature or time, a restriction is placed on the experimental range S(i,3,k) (Figure 3.2 p 21). A group of samples which could reveal diagnostic information regarding anticipated zero and first order reactions was selected for measurement of TG response characteristics.
Meaningful deductions can only be made from an analytical procedure which is founded on accepted scientific principles, even though in complex settings these may not always be individually obvious. The tests involve the computation of theoretical ML curves which should coincide with the observed ones if the reaction proceeded according to theory for eg a first order reaction. If the TG response is not in agreement with theory either the equipment or the analytical procedure may be erroneous. Positive results on the other hand would serve to indicate the overall accuracy and precision of the TG observations. This is in fact the way in which the equipment is calibrated.

To investigate a procedure by which TG mass loss curves can be directly compared to the laws of chemistry consider eg the first order reaction which was described by Hamill _et al_ (1960, p 315) for the decomposition of nitrogen pentoxide in carbon tetrachloride.

To simulate a hypothetical TG experiment assume that N_2O_4 stays in the solvent but oxygen is dispelled. If the container with the dissolved nitrogen pentoxide is visualized to rest on the pan of a TG mass balance set for a dispersion test, but without heat being applied, the data for a mass residue curve will be recorded which is proportional to that for the standard determination shown by Figure 3.26. The mass variations which are recorded need to be transferred into molar concentrations per liter of solvent to effect correspondence with the curve ANB in Figure 3.26.

The symbolic reaction,

$$2\,[N_2O_5] \;\text{--->}\; 2\,[N_2O_4] + [O_2] \qquad \text{R3.1}$$

at time t=0 mc 0 (gm mole/l)

at time t=t (mc-m) ---> mr m

shows the chemical change which occurs in relation to time. Disregarding the solvent, the initial mass = mc; the remainder N_2O_4 after time t elapsed = mr, and the mass of oxygen released = m, are also shown with the indication that a molar relation must be established. For this the reaction which occurs must be known.
In accordance with E3.6 where n = 1:
$d(mr)/dt = -k.mr$ ie for mr=mc at t=0; $mr=mc.\exp(-k.t)$ for N_2O_4, and $m=mc.(1-\exp(-k.t))$ for O_2.

For the smooth curves ANB and OMP constructed through the sets of data points, the points M and N can readily be picked as representing the end of the reactions for N_2O_4 and O_2. The "end of reaction" time, tb, amounts to 7250 s. Following the analysis for E3.9, the time 7250/5 = 1450 s represents the first natural period k.t = 1 ie the time required for completion of the reaction if the commencing rate of the reaction was sustained. The tangent at the origin, eg AX shows this condition for the N_2O_4 reaction.

The value for k, the rate constant, follows from 5/7250, ie 0,00066 s^{-1} . The stated value for k is 0.00067 s^{-1}. This shows that the analytical procedure is correct as derived for a first

$$2N_2O_5 = 2N_2O_4 + O_2$$

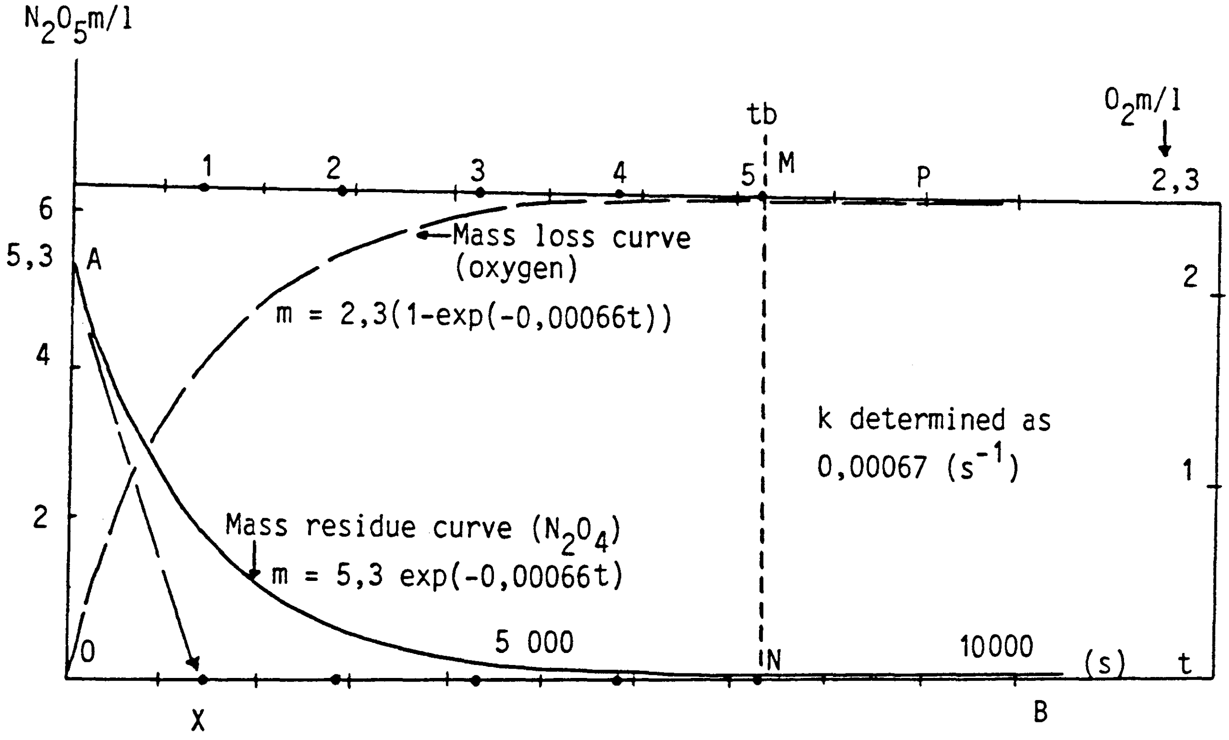


FIGURE 3.26 Decomposition of N_2O_5

order reaction such as R3.1. The MR or ML curves should therefore represent particular integrals for the differential equations, like E3.6, which govern the mechanism of the particular reactions which occur in the TG experiment.

3.5.3.1 Decomposition of carbonic acid

This reaction takes place at room temperature. Figure 3.27 shows the mass loss with time when 1,1432 g of commercial soda water, in a small flat container, is weighed at definite time intervals. The slight scattering of data points is due to the fact that bubbles of carbon dioxide did not always emerge immediately after formation, but coalesced and were then released disharmoniously with time. However an overall mass loss curve very similar to OM in Figure 3.26 is displayed.

The reaction rate becomes asymptotic after 1760 s when 17 mg CO_2 was liberated.
It follows that for the reaction:

$$H_2CO_3 \rightarrow H_2O + CO_2 \qquad R3.2$$

k = 1/352 s_{-1}, and the first order mass loss equation is:

$$m = 17.(1-\exp(-(t/352)) \qquad E3.1$$

Figure 3.27 indicates that the decomposition occurs in accordance with the standard equation for the rate of chemical reactions (E3.6), as the observed and computed exponential curves are very similar. The parabolic function is a much poorer fit. (Note that m is expressed in mg but since it is known that CO_2 is the product, it is simply required to apply a scale factor of m/44 for transferring to moles of carbon dioxide.)

It is therefore clear that the gravimetric component of TG analysis works well if the reaction conditions are right. Since the rate constant is known the "real" life time for soda water can be calculated. This demonstrates by analogy the need for the determination of the rate parameters and the form of the mass loss function in combustion analysis. By using the appropriate mathematical equations it is desired to predict the burn out times for different sizes of coal particles.

$H_2CO_3 = H_2O + CO_2$

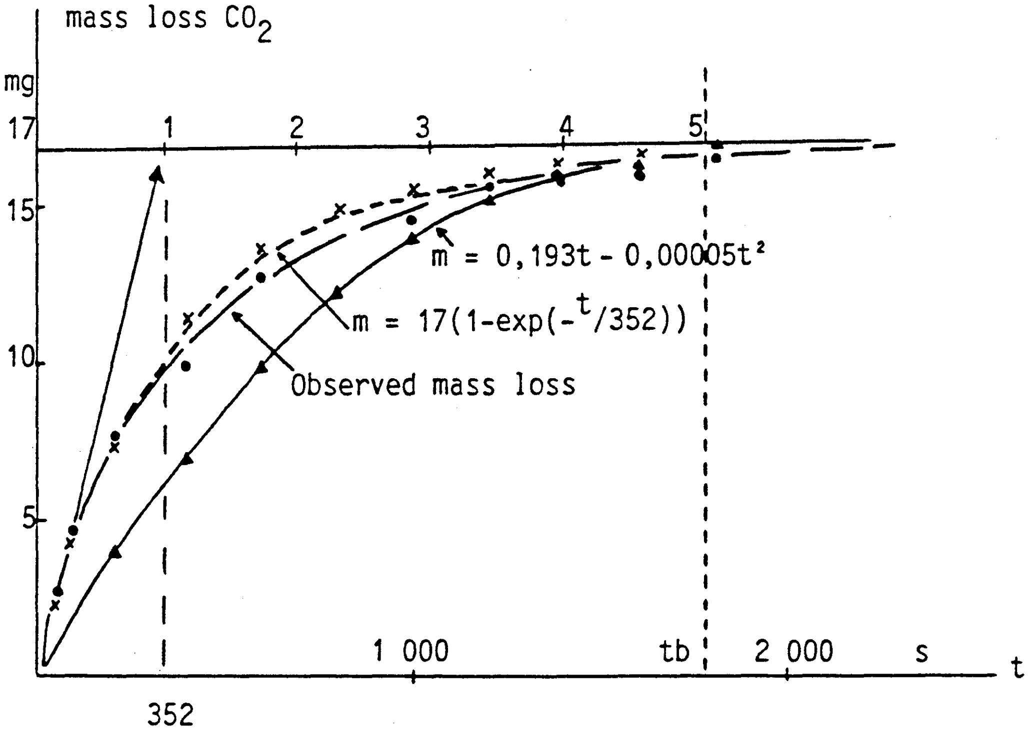


FIGURE 3.27 Decomposition of H_2CO_3 at room temperature

3.5.3.2 Burning of a high order paraffin

In this case the reactant must first be melted and then vapourised (both of which require latent heat) before combustion of the vapour takes place. Commercial solid paraffin of **unknown composition**, which ignites easily and reacts exothermally with a clear flame at high temperature, was studied by TG analysis. The sample is suddenly subjected to a high temperature environment with sufficient air. The heat is generated through reacting gases, after complete vaporization of the solid.

In Figure 3.28 three curves are presented viz. (1) The burn out (BO) curve, (2) The derivative of the BO curve, ie the DBO curve and (3) The near sample temperature superimposed on the ambient value of the furnace.

The change in mass was recorded at one second intervals and the following deductions can be made: the BO curve, oabcdef, displays a typical sigmoidal form but it is clearly of a segmented nature. This is also emphasized by the segmented nature of the DBO curve (OABCDEF), for which the BO curve represents the definite integral as defined by the segment limits.

The DBO curve displays four segments OAB, BC, CD and DEF. The first two corresponding segments of the burn out curve, oa and abc, are parabolic because their respective derivatives segments are linear. The third, cd, assumes a linear habit, (CD is almost horizontal), while the fourth def, could be regarded as the final natural growth function, when assessed in terms of E3.13, and the analysis of R3.1 and R3.2. (DEF represents a natural decay curve of the form $m = \exp(-kt)$.)

Initial decomposition takes place according to a chemical kinetic process which is not common in reference literature ie the BO phase segments cannot be identified in terms of functions which are solutions of E3.13. They would satisfy another type of rate equation which describes a different reaction process than E3.13. A zero order course then follows and finally a first order mechanism (combustion) is adopted to dispose of the mass.

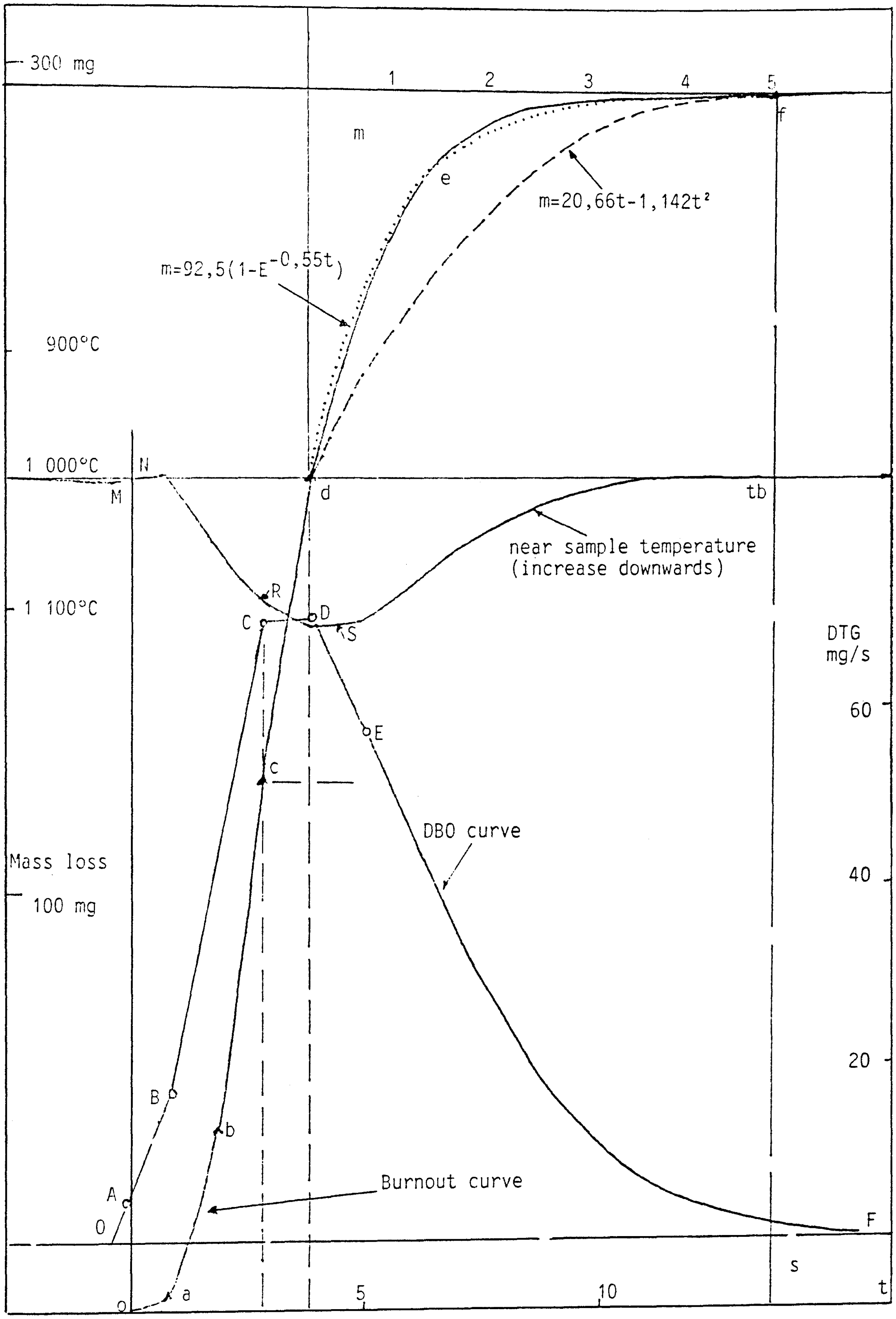


FIGURE 3.28 Burning of a high order paraffin

The near sample temperature shows that little heat is initially consumed at MN, probably for releasing the first vapour which is ignited at N. The temperature then rises and vaporization is enhanced from N to R. At R saturation appears to set in and equilibrium between combustion of vapour and its release is established from R to S. Reduced combustion then seems to set in, probably due to depletion of oxygen at the sample. The waning stage is then commenced and the temperature drops as the last fuel burns out.

The results indicate that the process for transforming the **solid fuel into a vapour** is not readily explainable in terms of standard reaction mechanisms using E3.13. The stage where combustion occurs however follows a standard course. This shows that different reaction mechanisms can be responsible for an apparently single event.

3.5.3.3 Decomposition of a potassium permanganate crystal within a hydrous solution of sulphuric acid and hydrogen peroxide

This reaction may have a possible resemblance to that of a carbon particle burning on its surface in the presence of air. In both cases the reaction probably takes place at a front which moves towards the center of the solid reactant, only the surface molecules are exposed to reaction and the inner ones must wait until they are exposed.

The rate of mass loss of the crystal determines the final reaction rate because potassium permanganate in solution reacts vigorously with hydrogen peroxide and sulphuric acid:

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \text{ --> } K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

The reacting medium was prepared by placing 40 g of water, 30 g of 0,1 N sulphuric acid and 26 g of about 15% hydrogen peroxide, along with 1 g of glass wool in a beaker which was tared on a weighing balance of 0,1 mg precision. The glass wool was spread out on the bottom of the beaker to support the crystal. In this manner all crystal surfaces were exposed for reaction. A potassium permanganate crystal of 0,085 g was dropped on the glass wool in the center of the beaker. From that instant onwards, the mass was recorded at regular intervals as for a normal TG experiment. A quantitative consideration of the standard reaction shows that the crystal should produce 4.3 mg of oxygen.

The observed results (Figure 3.29) indicate that a total mass loss of 3.8 mg was recorded: Some of the oxygen bubbles clung to the beaker. The reaction rate does not follow an exponential law; a much closer fit can be obtained for a parabolic expression of the form:

$$m = A.t - D.t^2$$

where $A = 0{,}362$; mg/s and $D = 0{,}000862$; mg/s^2.

This experiment distinctly shows that the reaction rate is controlled by the rate at which the crystal dissolves; this should be related to the rate of advancement of the reaction front, which in this case is probably less temperature dependent than in the case of carbon.
This test demonstrates that for some reactions an exponential law is not followed. In this regard the permanganate experiment is really instructive because the solution is coloured and the gas can be observed from the instant that it is evolved at the surface of the crystal. After a while a brown sludge encapsulated the crystal. This material, probably manganese oxide, did not dissolve by itself. Only when the solution was stirred at the end of the experiment did it dissolve quickly, demonstrating that a different level of activation energy was required for this reaction to occur.

The presence of this unreactive "cloud" could resemble the transport problem which occurs during combustion. The reaction products, mainly carbon dioxide and water vapour form a barrier between the reacting components viz. coal or char and oxygen. Practical combustion tests must therefore be carried out in air as the residual nitrogen is thought to perform a similar function. This seems to indicate that the damping parameter D, in the function, $m = A.t - D.t^2$, could possibly be related to the prevention of access of oxygen to the core of the particle. It also points to the need for turbulent in contrast to lamellar flow conditions for the feed of fuel into a PF furnace. This also explains why D depends on A: the faster the reaction, the

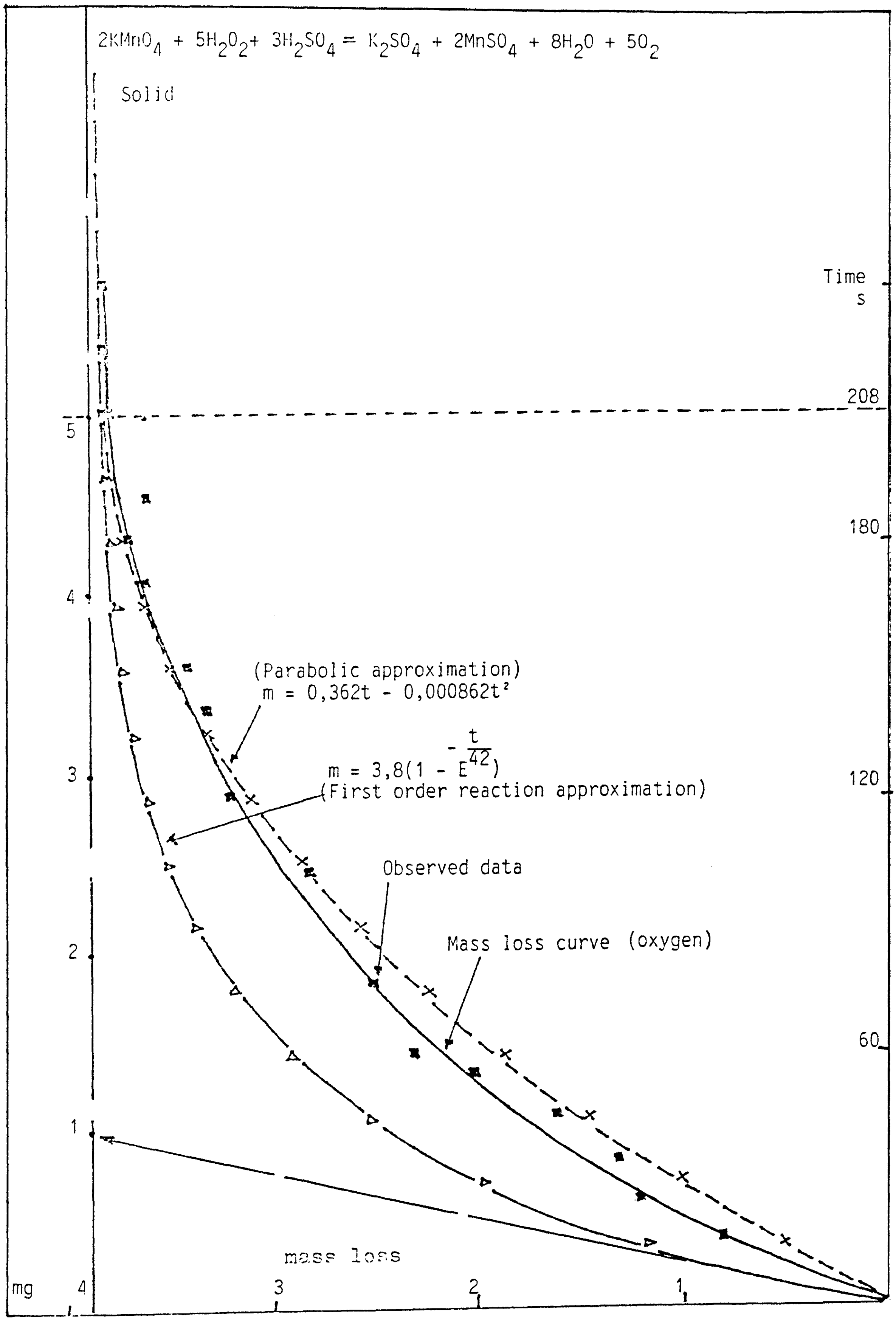


FIGURE 3.29 Solid reactant in a hydrous solution reacting medium

more products are formed to contaminate the reaction environment.

The fact that the results obtained with the TG equipment could be interpreted reasonably well, both qualitatively and quantitatively, proves that the recorded data are reliable.

3.5.3.4 Direct decomposition of various solid state inorganic compounds

These experiments represent endothermic reactions of solids, eg dehydration and dissociation.

Figure 3.30 shows the dispersion ML curves of copper sulphate, calcium carbonate and of lime that had been exposed to air, ie a mixture of calcium hydroxide and calcium carbonate. The reactions of these compounds are considered to be even closer analogies to the reactions expected for coal during TG analysis because they take place at high temperature. The decomposition is effected according to S(1,3,2) ie dispersion analysis of chemical reactants. The tests are carried out over extended time so that equilibrium can be attained between heat supply and completion of the thermal effects. This ensures that the anticipated reactions will in fact occur so that they can also serve as a means of calibrating the system.

The masses computed for the specific reaction products according to theory () and those derived from the TG data are shown in Figure 3.30 in tabulated form. The close correspondence shows that the equipment performs satisfactorily.

A. Decomposition of copper sulphate.

The decomposition of copper sulphate, (approximate 1,5mm crystals), emulates a coal dispersion which extends from low to high temperature decomposition. It is clearly demonstrated by the linear DTG curve segments (Figure 3.31), that the mass loss does not follow an exponential function. After evaporation of surface water four moles of water of crystallization are lost as an almost continuous process. A slight deflection shows that the

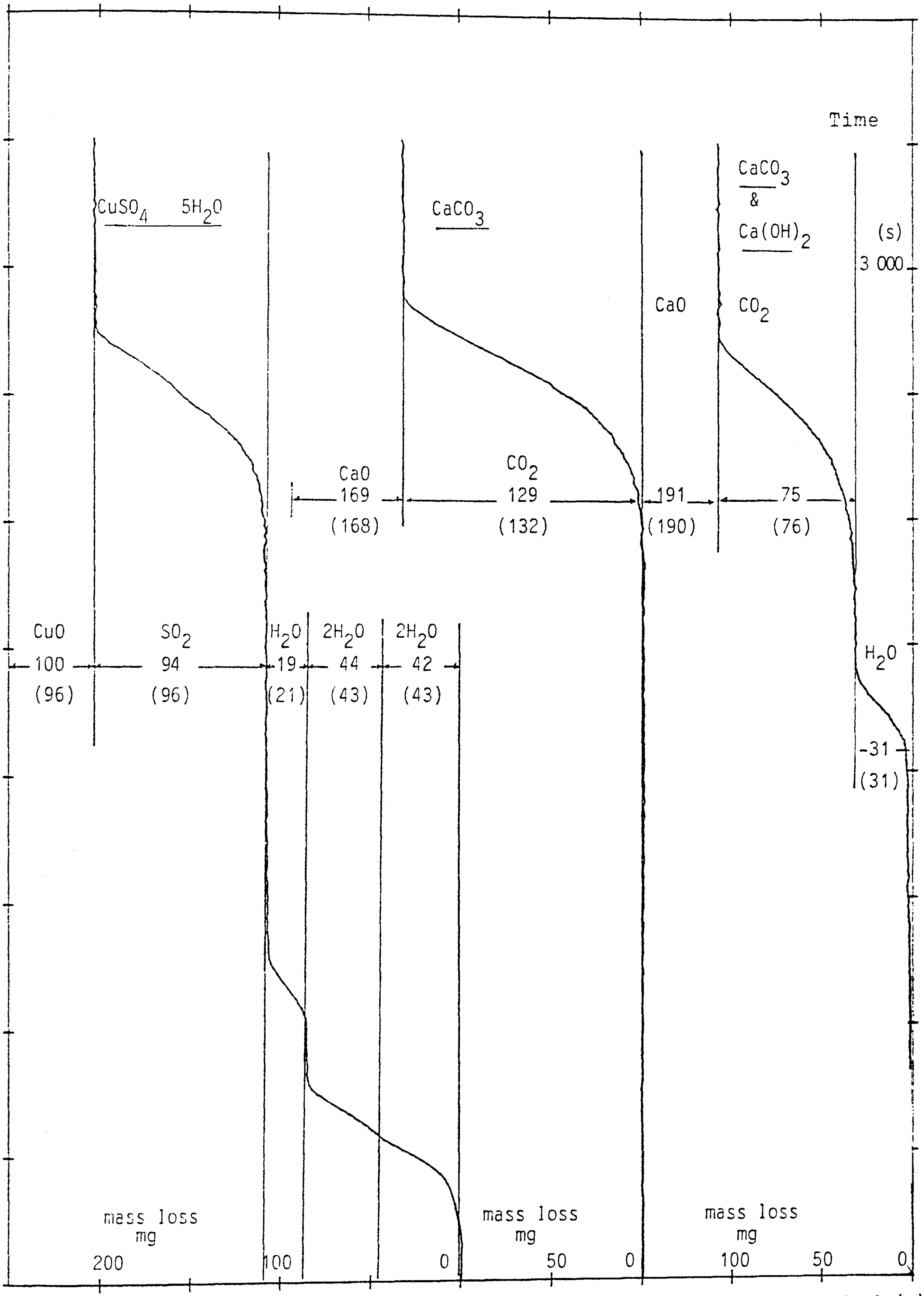


FIGURE 3.30 The quantitative deomposition of various inorganic solids. Theoretical ( ) vs observed values of mass loss.

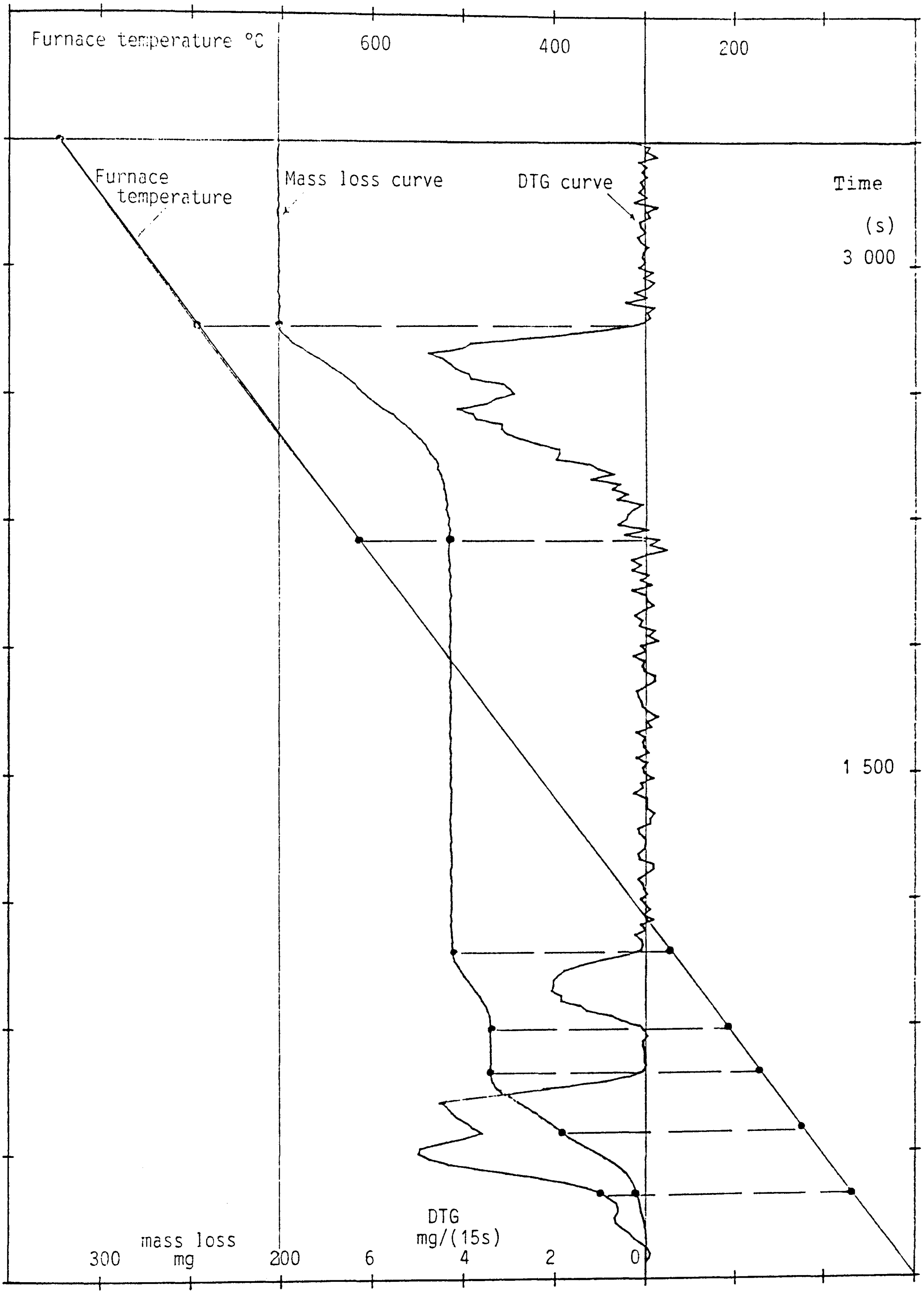


FIGURE 3.31 The phase structure for decomposition of copper sulphate

process represents two phases where two moles are released in succession. The fifth mole of crystal water is expelled at a much higher state of thermal activation. Why the release of sulphur trioxide occurs in definite phases (see the DTG curve) is not known. The entire reaction is endothermic and the phase temperatures are directly related to the furnace temperature.
Through application of S(2,3,k) any particular phase can be reconstructed for detailed analysis.

B. Decomposition of calcium carbonate.

Figure 3.32 shows the temperature range over which calcium carbonate, in very fine powder form, decomposes into CaO and CO_2. The expected natural growth curve OMR of a first order reaction, (dashed) does not agree with the observed ML curve OPR.

The mass loss curve does not follow an exponential law: it appears very likely that decomposition of a grain of calcium carbonate, although its temperature may be above about 600°C, progresses from the outside towards the center in the form of a reaction front, similar to the migration of a flame front in the case of burning carbon or even more appropriately coal: the fringe of calcium oxide which forms around the carbonate core of the grain, may simulate the role of ash which encapsulates a coal particle.

C. Decomposition of a mixed calcium hydroxide and calcium carbonate.

Figure 3.33 shows that TG can be used to determine the percentage of calcium carbonate which formed by exposure of calcium hydroxide to air. The decomposition of hydrated lime occurs within the exothermal range of normal coal ie around 400°C. If present in coal its effect will be superimposed on the mass loss curve for the coal and will probably be obscured. (The water vapour in this case will gather with the volatiles and form a component of VM ie mv, in a standard analysis.) The carbonate decomposition (iv) is initiated at a temperature which is higher than that of the burning carbon in a dispersion experiment and

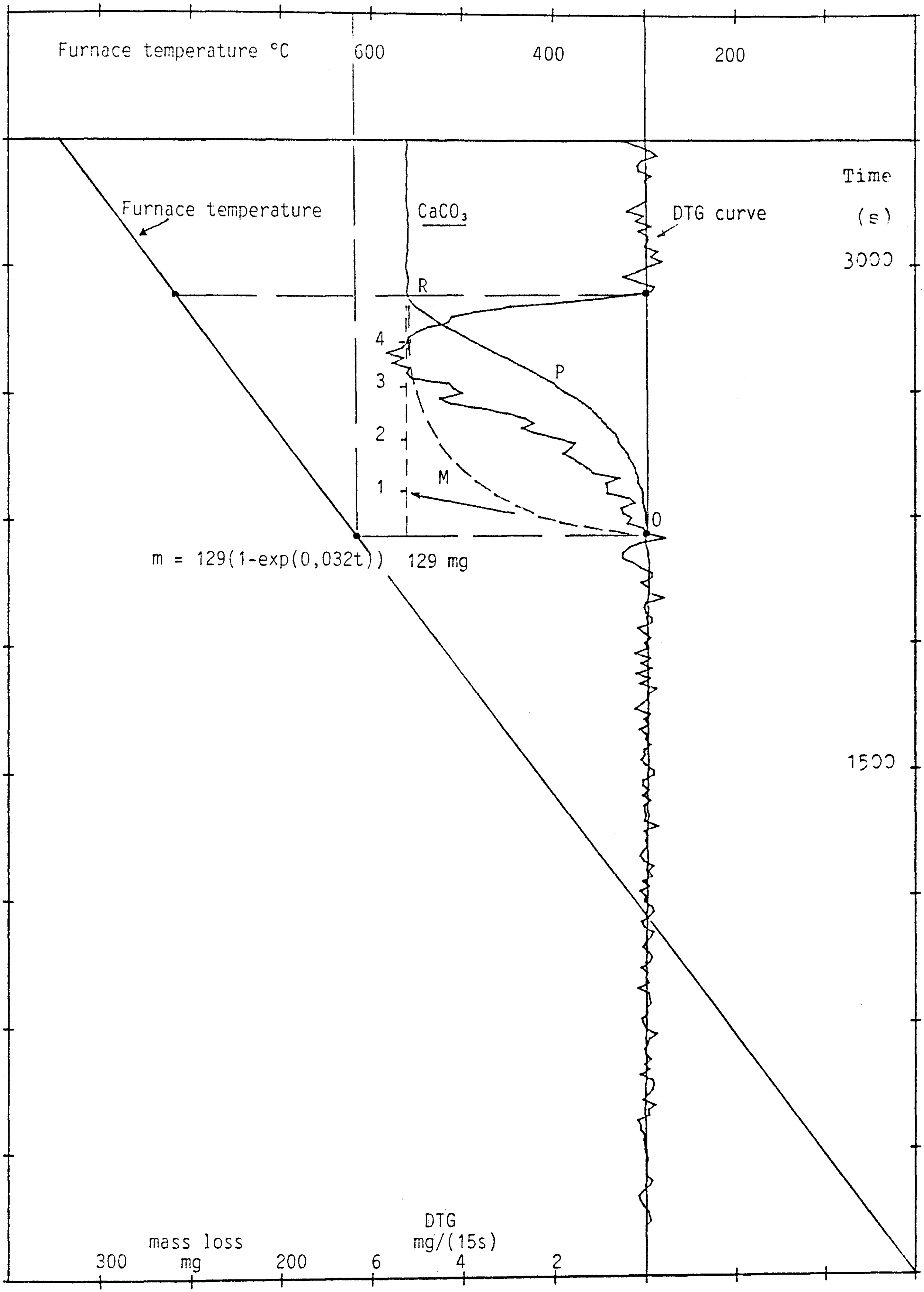


FIGURE 3.32 Kinetic parameter and phase structure for decomposition of calcium carbonate

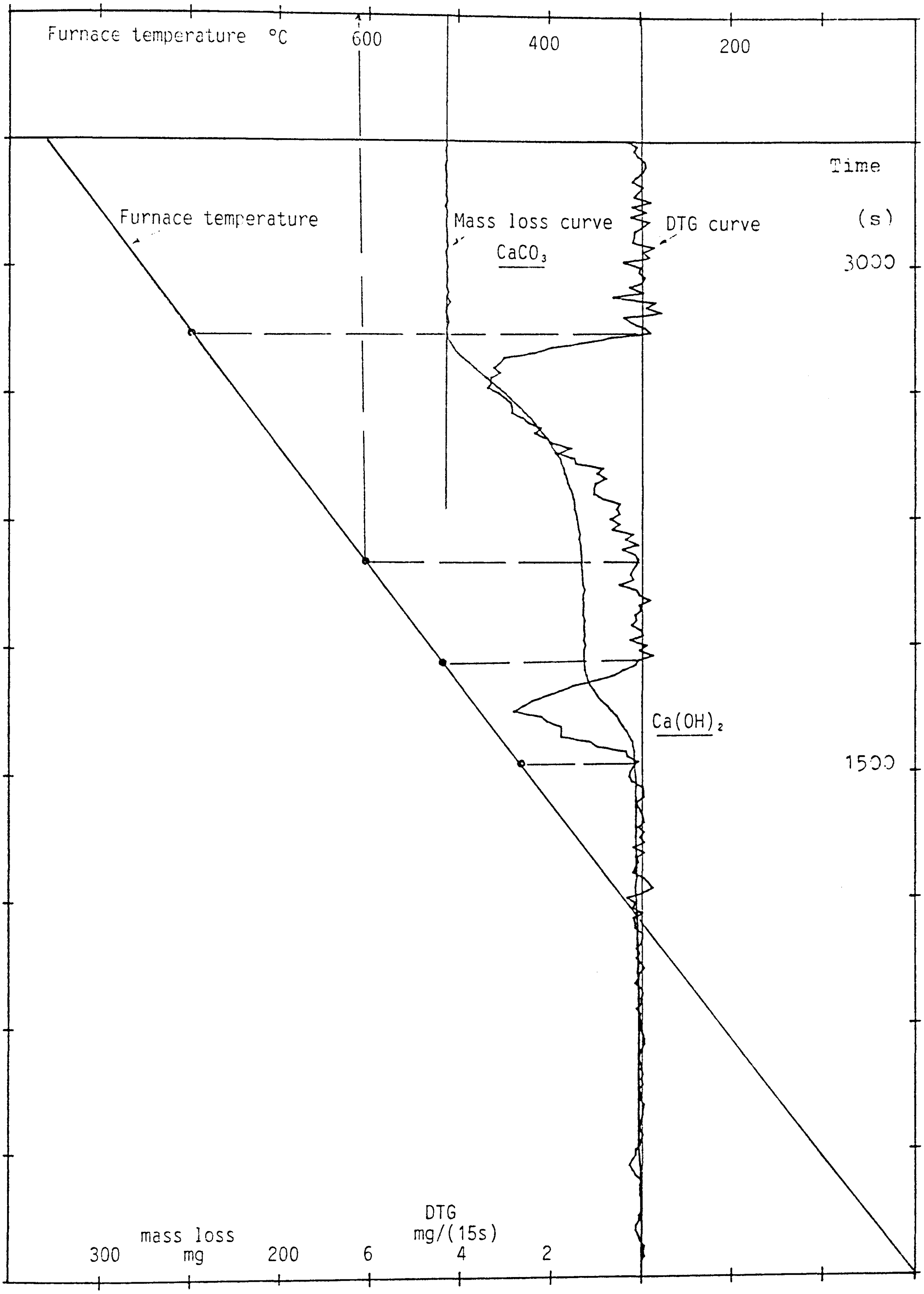


FIGURE 3.33 The dispersion structure for mixed $CaCO_3$ and $Ca(OH)_2$

can thus be identified. This illustrates the case for heterogeneous multicomponent reactions.

3.5.3.5 Concluding remarks

The TG tests with pure chemicals confirm that the mechanisms of decomposition of a solid follow specific laws. This should be taken into consideration before assumptions regarding a basis for interpretation of results are made. Results regarding activation energies for coals, based on the prescripts of the law of mass action without due consideration, could therefore be speculative. Various ways for computing activation energies of coals from TG data are possible but their utility can only be assessed after a sufficient number of coals has been analysed.

4 TG ANALYSIS OF SOME SOUTH AFRICAN COALS

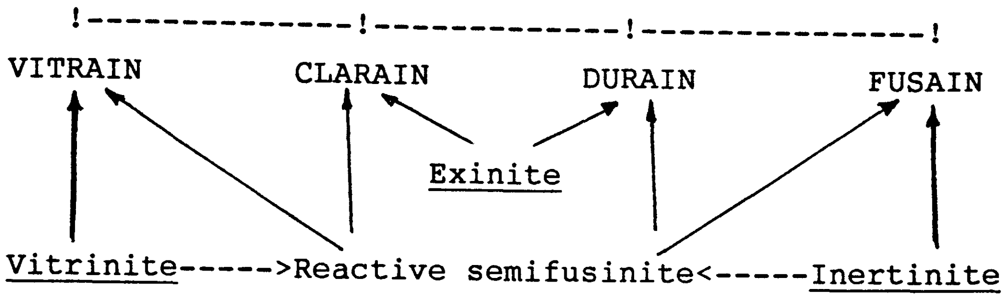
For the precise evaluation of the thermal response of coal it is essential that the coal should be characterized in terms of the material which it contains. Various systems (proximate and ultimate analysis, petrography) are in existence but it is difficult to integrate any of these with the results of TGA, or to correlate them with the burning properties of coal.

A system which lends itself to this objective was described by Snyman *et al* (1983). This system has the advantage that it not only provides a quantitative basis on which coal can be "classified" but it also provides supplementary attributes for "specifying" the coal so that coal can be identified with even greater precision, depending on the particular contribution a specific analytic technique can make. Specific constituents of coal can be correlated with burning characteristics.

To establish a basis for detailed classification of coal attention should be focused on its inner fabric, grain and composition. An abstract of this approach was amongst others, presented by Snyman (1976, p 242-252). Aspects of this exposition, which are of importance regarding the use of TG techniques for the specification of coal, are presented for convenient reference.

To the unaided eye a lump of coal consists of layers of dull and lustrous black material. Further details are only recognizable with the aid of a microscope. Identifiable organic entities can be grouped as shown by Table 4.1.
The lithotypes are related to the maceral groups in the following manner:

LITHOTYPES



With these closely interlinked associations it is difficult to separate pure components for individual analysis.

Lithotypes fall within the millimeter range of stratification and microlithotypes within the micrometer range. If a coal is thus broken down to a grain size within the millimeter range, a single particle generally represents a single lithotype but even within the 0.1 mm range, it will in most cases not be fine enough to represent individual macerals. TG response, which is grain orientated, (-70 mesh, -0,210 mm) can normally be expected to reflect the integrated response of microlithotypes such as vitrite, clarite and inertite. In South African coals the exinite content seldom exceeds 5%, and clarite is also not present in substantial amounts. The same applies to trimacerite, durite, fusite and semifusite.

Interpretations based on well defined coal compositions in terms of the main maceral groups, (ie vitrinite, exinite and inertinite) are believed to be the most promising for developing TG based specifications for coal. A chance exists that reasonably pure concentrations of these groups can be attained.

TABLE 4.1

A Grouping Scheme for Coal Based on Maceral Composition

(Vi = Vitrinite   Ex = Exinite   In = Inertinite)

Megascopical observation	Microscopic observation	
Lithotypes	Microlithotypes	Maceral Groups
VITRAIN (bright)	Vitrite	> 95% Vi
FUSAIN (fossil char)	Fusite Semifusite	>95% Fusinite >95% Semifusinite
CLARAIN (semi-bright)	Clarite Trimacerite	>95% Vi + Ex Vi + Ex + In
DURAIN (mat black)	Durite Inertite	>95% In + Ex >95% In
BOGHEAD COAL (brown)	(torbanite)	Ex + In
CANNEL COAL (black)		Ex + In

By studying TG responses in relation to microlithotype or maceral composition the identification of specific diagnostic form features which may be displayed by the TG curves could possibly be interpreted. The TG derived specification parameters will form the basis for comparing the coals in preference to other analytic procedures such as eg Fourier analysis of the ML curves.

4.1 The Grade/Type/Rank (GTR) classification of coal

A classification system with which TGA can most effectively be integrated should possess the following characteristics:

1. All parameters must be quantified.
2. Regression trends between variables should follow simple mathematical functions.
3. Constraints in terms of deviation limits must be expressed in numbers.
4. All parameters required for a complete classification must be derivable from a single TG experiment.

A report by Snyman et al (1983) not only meets the requirements for controlled TG interpretation very well, but allows the use of TG dispersion analysis as a means for adding **specification parameters** (op cit, p 53), which are related to the observed thermal response characteristics of the classified coal.

After considering several ways of classifying coal, Snyman et al (1983, p 53), concludes: "It is therefore essential to classify coal in terms of its grade, type and rank. The moisture-free ash content is regarded as a parameter of grade, whereas the inferred vitrinite content and inferred Rovmax (as derived from any two suitable chemical properties by means of Fig 7) are parameters of type and rank. Such a classification code in terms of grade/type/rank can serve to evaluate other possible fields of utilization,......". Further on (op cit, p 56), the defining requirements are outlined: "The only analytical requirements are the calorific value, and the proximate analysis in terms of moisture, ash and volatile matter contents. The dry ash free calorific value and volatile matter contents can readily be calculated and the intersection determined on the proposed Seyler diagram modified for South African coals".

Concerning extended properties it is concluded (op cit, p 59): "Other coal properties which are largely determined by the inorganic constituents cannot be accommodated in such a grade/type/rank classification system and should be regarded as specifications". Finally, with regard to further research it was envisaged (op cit, p 60): "(2) the optimizing of the relationships between the grade type rank of coal and other important parameters, eg ..... (b) combustion characteristics (combustion profiles)".

4.2 The selection of test samples

In order to explore possible relationships between coal properties and the results of thermal analysis, a group of representative coal products, to serve as test samples, were selected to cover as far as possible, the total range of coals available in the RSA. A total of 22 coal products, varying in grade/type/rank were studied to establish how results from TGA compare with laboratory determined values and to determine what additional information could be derived. The approximate geographic distribution of the sample products is shown on Figure 4.1 and a list of the collieries is given in Table 4.2.

The manner in which the selections were made can be observed with reference to Figure 4.2. It represents the modified Seyler Chart, op cit (1983, Figure 7), with the vitrinite and % Rovmax isopleths approximated by straight lines to facilitate computer programming. The fundamental co-ordinates have also been altered so that positive numbers fall in the first quadrant as conventional. This transformation simplifies algorithm specifications for isopleth constraints as it eliminates the use of negative numbers.

Figure 4.2 can be regarded as an alpha-numeric array which is formed by two sets of oblique coordinates, ie the type and the rank boundary lines respectively, within the GTR matrix. The schematic arrangement of coal samples displaying coordinated group characteristics, is shown by a hypothetical coal group

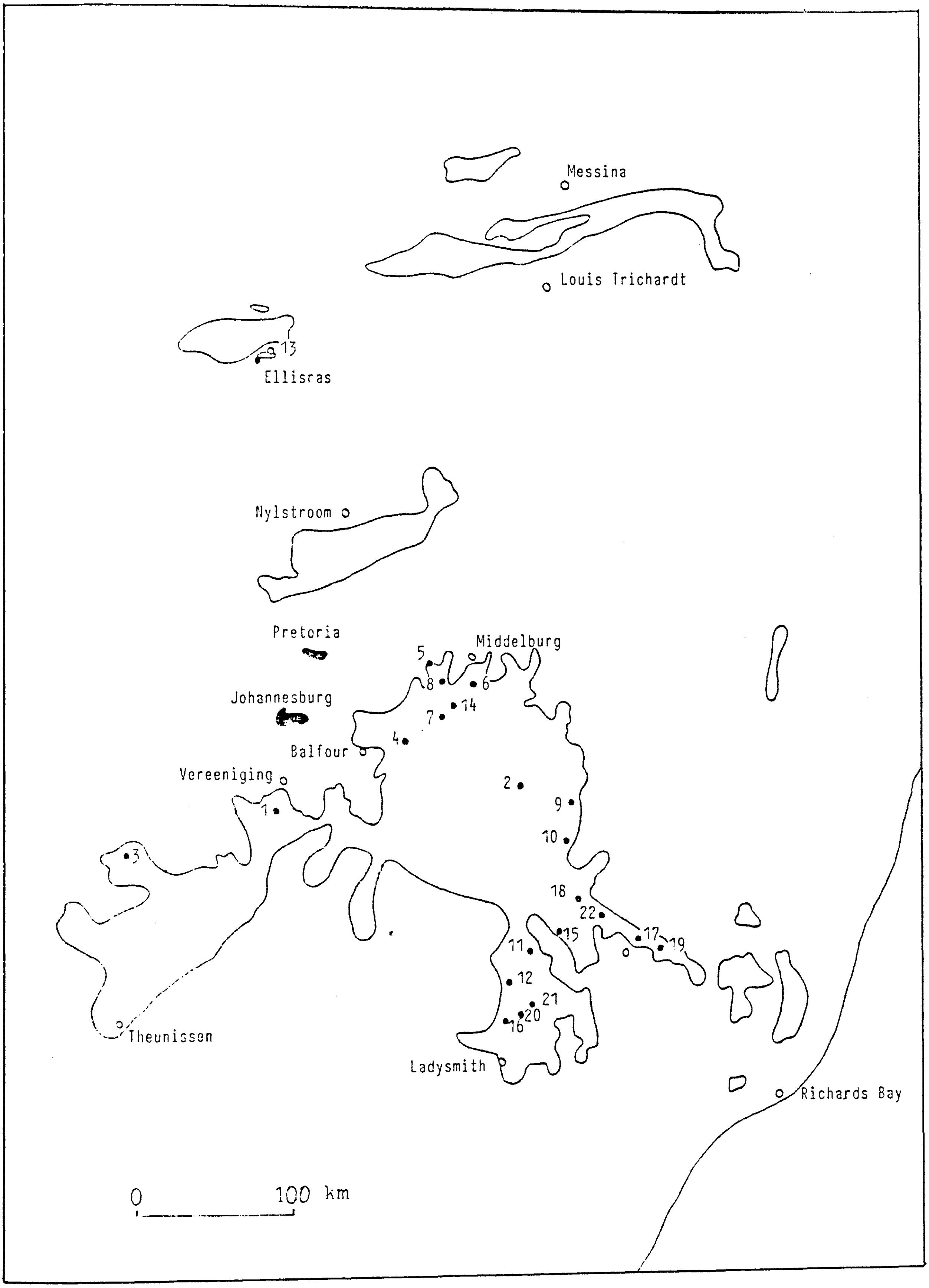


FIGURE 4.1 Distribution of the range of test samples

TABLE 4.2

COLLERIES AND TYPES OF COAL USED FOR TEST ANALYSIS

			Classification		
S.#	Mine	Product	Symbol	Actual	Coal type
1	Sigma	+ 12mm	V/D/0	286/31/061	Bituminous
2	Kobar	Nuts	III/D/3	176/22/094	Bituminous
3	Vierfontein	Crushed coal	V/D/0	258/31/074	Sub-bituminous
4	Delmas	Nuts	III/C/0	192/41/067	Bituminous
5	Kleinwater	Nuts	II/D/0	137/34/071	Bituminous
6	Bank 5	Nuts	II/B/1	121/64/078	Bituminous
7	Arthur Taylor	Nuts	II/D/0	128/32/075	Bituminous
8	Greenside	Peas	III/D/1	156/27/078	Bituminous
9	Spitzkop	Peas	III/C/0	173/48/068	Bituminous
10	Usutu West	Crushed coal	V/C/0	272/54/065	Bituminous
11	Zimbutu	Nuts	II/C/0	144/42/074	Bituminous
12	Ballengeich	Nuts	III/C/0	196/44/074	Bituminous
13	Grootegeluk	Coking	II/A/0	102/90/065	Bituminous
14	Springbok	Small nuts	II/D/1	106/40/076	Bituminous
16	D.N.C.	Coking	II/C/2	115/51/085	Bituminous
15	Utrecht	Nuts	II/C/9	138/42/210	Anthracite
17	Vryheid Coronation	Coking	III/D/5	177/34/113	Anthracite
18	Longridge	Nuts	II/C/8	115/44/194	Anthracite
19	Natal Anthracite	Nuts	II/D/8	130/33/198	Anthracite
20	Springlake	Grains	II/C/9	125/48/275	Anthracite
21	Nonsana	Nuts	II/C/9	145/49/252	Anthracite.
22	Brockwell Anthracite	Nuts	II/C/9	118/43/354	Anthracite

S.# = Sample reference number
Classification based on microscopy and laboratory determined ash values

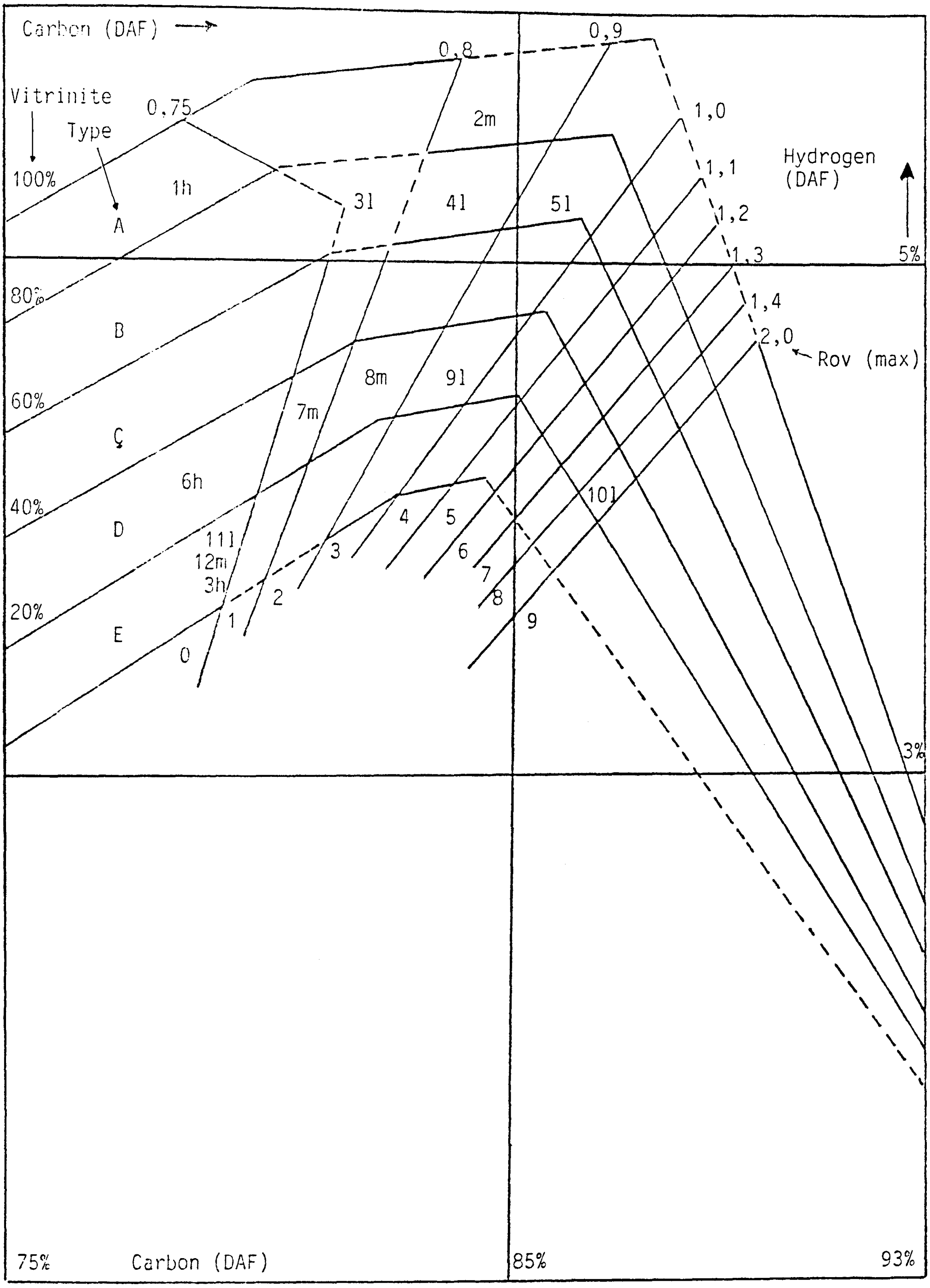


FIGURE 4.2 The adapted Seyler nomogram approximated with linear isopleths

represented by a sequence of numbers, eg 2m, 41, 8m. These are plotted on the distorted vitrinite- % Rovmax, alpha-numeric indexed array, commonly known as a "Seyler Nomogram". The position of a sample is determined by its daf carbon and hydrogen contents, ie the orthogonal prime co-ordinates of the first quadrant are used. The point, representing a specific coal, will fall within an area contained by Rovmax and % vitrinite as its boundaries are also defined in terms of the prime co-ordinates. Constraints are shown on Tables 4.3 and 4.4 which refer to Snyman op cit (1983, p 58 and table 20).

Since a plotted point, or the number representing the point, can be grouped within a tessera defined by type and rank it can be indexed as shown in Figure 4.2, eg coal 1h is represented by row A and column 0. The effect of the classification diagnostics is that solely for reference purposes, the sample can equally well be represented by a square matrix, A(t,r), (Figure 4.3), for which the alphabetical indexes (left side) are interchanged with numbers (right side) for the sake of convenience. This mosaic is defined by ranges of vitrinite %, and rank, as rows and columns, respectively.

A(t,r), eg A(1,0), will designate all coals with vitrinite contents ranging between 0 and 20%, and Rovmax % values smaller than 0,75. It should be noted that the C and H axes, which define these percentages, are oblique with respect to A(t,r); hence the actual plotting must be done using the prime co-ordinates of Figure 4.2, on which the algorithm for computerization is also based. The square array, like the square matrix to follow, is only introduced for convenience to facilitate the formation of a simple mental image of the process.

The distribution of the hypothetical coal samples shown schematically in Figure 4.2 implies that the systematic variation of classification parameters (or matrix indexes) in a coal sequence, **amongst others**, can effect the TG dispersion curve:

1. For eg A(t,2), (refer Figure 4.3) the hypothetical sample

TABLE 4.3

If the need should arise (e.g. for the subdivision and proper evaluation of coal reserves) these classes can be subdivided by means of small increments of grade (which can be denoted by Roman numerals, e.g. I to V), type (which can be denoted by A to E) and rank (which can be denoted by 0 to 9).

The following increments are proposed:

Grade		(percentage ash - dry basis)	
I	(l)	< 10	1
II		10 - 15	
III	(m)	15 - 20	2
IV		20 - 25	
V	(h)	25 - 30	3
VI		30 - 35	
VII		> 35	

Type	(percentage inferred vitrinite)	
A	> 80	5
B	60 - 80	4
C	40 - 60	3
D	20 - 40	2
E	< 20	1

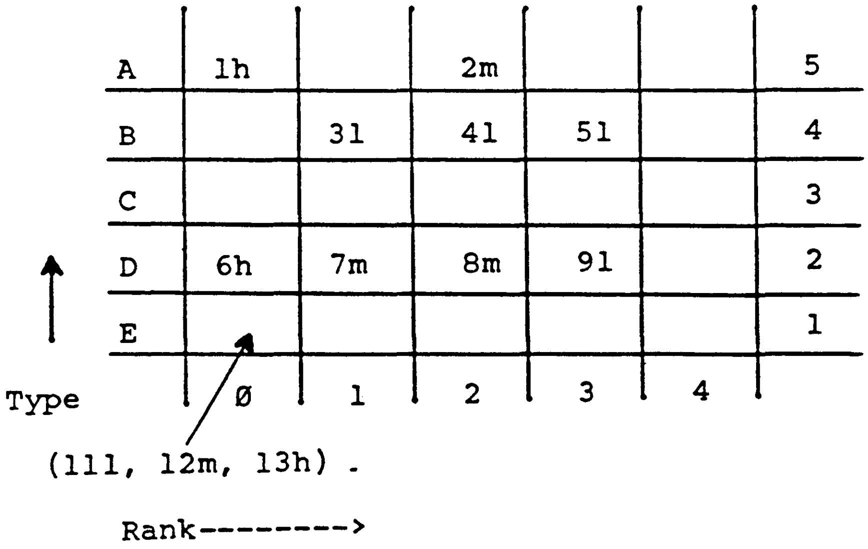
Rank	(inferred Rovmax, per cent).		
0		<	0,75
1	0,75	-	0,80
2	0,80	-	0,90
3	0,90	-	1,00
4	1,00	-	1,10
5	1,10	-	1,20
6	1,20	-	1,30
7	1,30	-	1,40
8	1,40	-	2,00
9		>	2,00

TABLE 4.4

A PROPOSED RANK CLASSIFICATION FOR SOUTH AFRICAN COAL

Class	Sub-bituminous coal	Bituminous coal	Lean coal	Anthracite
Rovmax %	≤ 0,75	> 0,75 ≤ 1,40	>1,40 ≤2,00	> 2,00
Volatile matter (daf) %	24 - 48	18 - 45	11 - 22	< 15
Cal. Val. (daf) MJ/kg	< 33,5	29,2 - 37,0	32,8 - 36,6	32,8-36,3
Coking properties	-	±	-	-

+ present; - absent.



	0	1	2	3	4	
A	1h		2m			5
B		3l	4l	5l		4
C						3
D	6h	7m	8m	9l		2
E						1

l = low % ash   m = medium % ash   h = high % ash

FIGURE 4.3 A schematic reference Type/Rank array A(t,r sequence 2m, 4l, and 8m of rank 2, and of similar grade (ash varying only slightly from low to medium ie l to m), the vitrinite content, should essentially be responsible for variations in the TG dispersion curve because it represents the sole variable ranging from type A to D. (Ideally ash should be zero or constant.)

2. For eg A(2,r), Figure 4.3 the series 6h, 7m, 8m, and 9, of type D, with rank variations 0, 1, 2 and 3, rank should have the main effect on the TG response. (The ash must remain reasonably constant. However in the sample series the ash content varies from low to high ie a range from 10% to 35% which is undesirable but unavoidable).
3. For a sample series of constant type and rank, Figure 4.4 changes in the ash content should have the greatest effect on the TG response. Illustrated in the two dimensional array eg A(1,0) the series 11l, 12m and 13h, of type index E and rank 0, represents the case where ash content is low, medium and high.

Since the Grade/Type/Rank classification comprises three variables, a three dimensional array, referred to as a GTR matrix, is required to index all three variables in terms of specific constraints. This is shown by Figure 4.4, where ash constraints are presented on the grade axis according to Table 4.3 as originally specified.

The original grade specifications (Snyman et al, 1983) contain seven stack blocks (Figure 4.4 and Table 4.3). To provide only for low (l=10-15%), medium (m=15-25%), and high (h=25-35%), ash contents ie subscripts 1, 2, 3, the original seven grades need to be reduced to three to allow larger tolerances on the grade to reduce the number of groupings (see modifications in Table 4.3.) In order to provide for this third dimension on the two dimensional array of Figure 4.3 the sample designations, (Figures 4.3 and 4.5), are subscripted (symbolically) by l, m or h, to comply with the ash content.

The distribution of the test samples, according to their classifiction symbols, (Tables 4.2, 4.4, 4.5 and 4.6) are shown in array format by Figure 4.5. The overall distribution of the

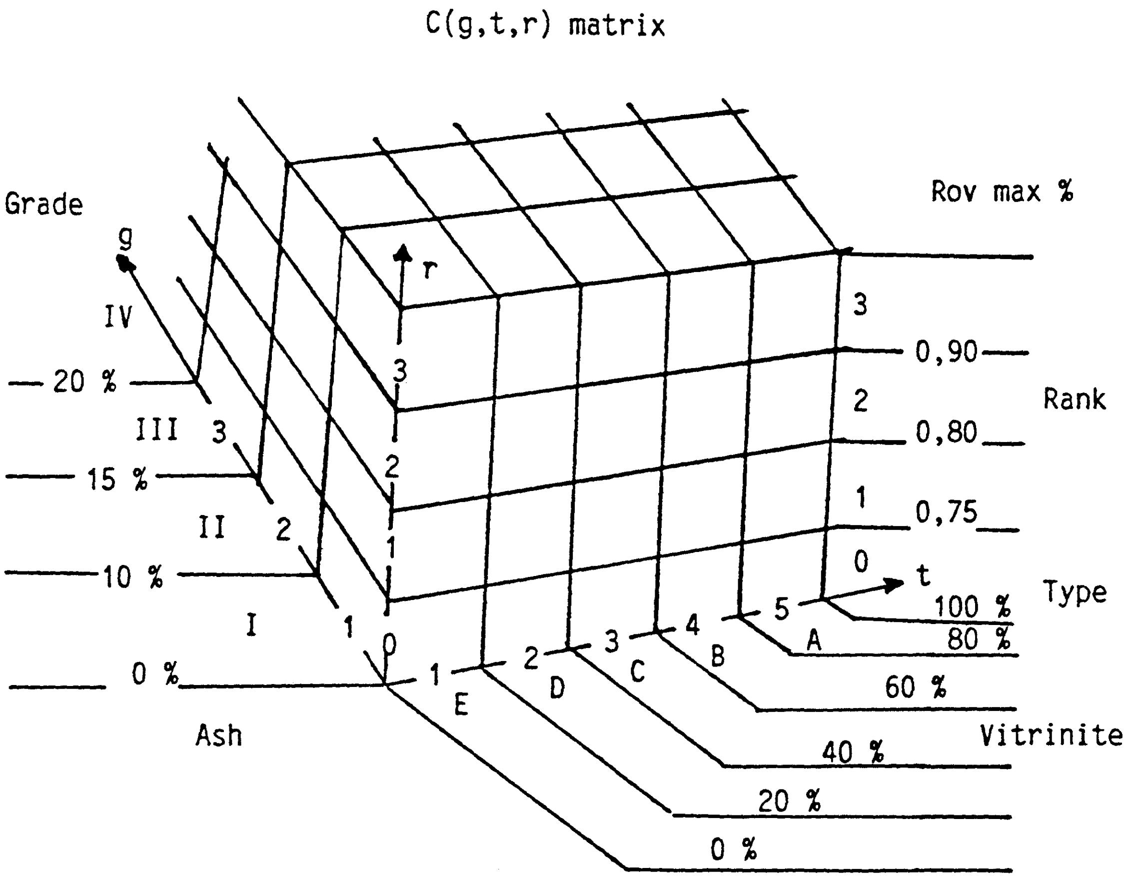


FIGURE 4.4 The grade/type/rank matrix

TABLE 4.5

MACERAL ANALYSIS FURNISHED BY DIE NICR PETROGRAPHICAL LABORATORY

S. #	Vitrinite (%)	Exinite (%)	Reactive semi fusinite (%)	Inertinite (%)	Visible minerals (%)	Rov max (%)
1	25,0	3,3	12,9	40,4	18,4	0,61
2	19,9	2,1	32,3	37,3	8,4	0,94
3	25,9	2,1	13,9	42,7	15,4	0,74
4	38,4	7,2	15,5	32,7	6,2	0,67
5	33,0	9,0	15,0	39,8	3,2	0,71
6	61,8	7,8	7,4	19,9	3,1	0,78
7	30,9	6,7	20,6	37,8	4,0	0,75
8	25,4	4,7	20,3	44,3	5,4	0,78
9	44,7	6,2	11,7	30,4	7,2	0,68
10	46,0	5,6	9,2	25,2	14,0	0,65
11	39,7	5,0	15,3	35,3	4,7	0,74
12	40,2	5,5	14,4	31,5	8,4	0,74
13	86,8	4,8	1,4	3,3	3,7	0,65
14	38,4	5,5	18,4	34,6	3,1	0,76
16	49,4	4,3	15,4	27,8	3,1	0,85
15	40,0	0,0	21,8	33,1	5,1	2,10
17	32,3	1,6	26,5	35,2	4,4	1,13
18	40,1	0,0	19,9	31,5	8,5	1,94
19	31,1	0,0	29,8	32,0	7,1	1,98
20	44,7	0,0	15,0	33,6	6,7	2,75
21	46,0	0,0	15,0	33,0	6,0	2,52
22	41,3	0,0	15,0	39,4	4,3	3,54

S. # = Sample reference number

Rov max = Reflectivity of vitrinite in oil

TABLE 4.6

MACERAL ANALYSIS OF SAMPLES, MINERAL MATTER FREE (mmf) VALUES

S. #	Vitrinite (%)	Exinite (%)	Reactive semi fusi-nite (%)	Inertinite (%)	Rov max (%)
1	30,6	4,0	15,8	49,5	0,61
2	21,7	2,3	35,3	40,7	0,94
3	30,6	2,5	16,4	50,5	0,74
4	40,9	7,6	16,5	34,8	0,67
5	34,0	9,3	15,5	41,1	0,71
6	63,7	8,0	7,6	20,5	0,78
7	32,1	7,0	21,4	39,3	0,75
8	26,8	5,0	21,4	46,8	0,78
9	48,1	6,7	12,6	32,7	0,68
10	53,5	6,5	10,7	29,3	0,65
11	41,6	5,2	16,0	37,0	0,74
12	43,8	6,0	15,7	34,9	0,74
13	90,1	5,0	1,5	3,4	0,65
14	39,6	5,7	19,0	35,7	0,76
16	50,9	4,4	16,0	28,7	0,85
15	42,1	0,0	23,0	34,9	2,10
17	33,8	1,6	27,7	36,9	1,13
18	43,8	0,0	21,7	34,4	1,94
19	33,4	0,0	32,0	34,4	1,98
20	47,9	0,0	16,0	36,0	2,75
21	48,9	0,0	15,9	35,1	2,52
22	43,1	0,0	15,6	41,2	3,54

S. # = Sample reference number
Rov max = Reflectivity of vitrinite in oil

Rank -------------->

	0	1	2	3	4	5	6	7	8	9	Type
A	13	[1]	////	////	//	/////	//	//	////	///////	5
B	6	/////	////	////	//	/////	//	//	////	///////	4
C	[10] (9) (11) (4) (12)	///// ///// /////	16	//// //// ////	// // //	///// ///// /////	// // //	// // //	18	15, 21 20, 22	3
D	7, 5,[3] [1]	14 (8)	//// ////	(2)	// //	(17)	// //	// //	19	/////// ///////	2
E	//////////	/////	////	////	//	/////	//	//	////	///////	1

Ash %: l = sample number eg. 14, m = sample number eg. (2).

h = sample number eg. [3]

/////// = absent coal class

FIGURE 4.5 Classification of a group of test samples according to rank and type

samples is not entirely satisfactory because of the many gaps which cause discontinuities of sequences.
In order to incorporate coal as a classified reactant into the TG experimental state matrix the S() matrix must be extended to incorporate the C(g,t,r) matrix which is referred to as the classification matrix.

It follows that for each TG technique, as specified by the S() matrix, there are C(g,t,r) coal types available as reactants. All the diagnostic parameters required for establishing C(g,t,r) ie the coal classification can be determined from a single TGA test on a given coal sample (See 3.3.1.1 p 25 to 3.3.1.3 p 31). Besides the extended quasi proximate analysis, all the thermal parameters, as well as information about the vitrinite content and rank of a coal can be given from TG data, if the algorithm for resolving the Seyler nomogram can be established. Figure 4.2 illustrates the basis for this algorithm which can be improved upon by considering the data furnished by Barnard (1987).

Snyman _et_ _al_ (1983) also furnished formulae for computing ultimate analysis values, total carbon and other useful parameters sush as the Hardgrove index (HGI).

4.3 An analysis of the dispersion DTG curves of a set of reference coals

The DTG curves for all the test samples are presented in Figures 4.6 to 4.11. In order to illustrate the variation in curve features, due to specific variables, (Figure 4.5) only the required sequences of DTG curves are plotted and presented as groups in Figures 4.12 to 4.16 to facilitate discussion.

4.3.1 Influence of rank variation

Following the classification matrix, (Figure 4.5), the type-D series, C(?,2,r), (20%-40% vitrinite) will be considered first and then the type-C series, C(?,3,r), of coals. The manner in

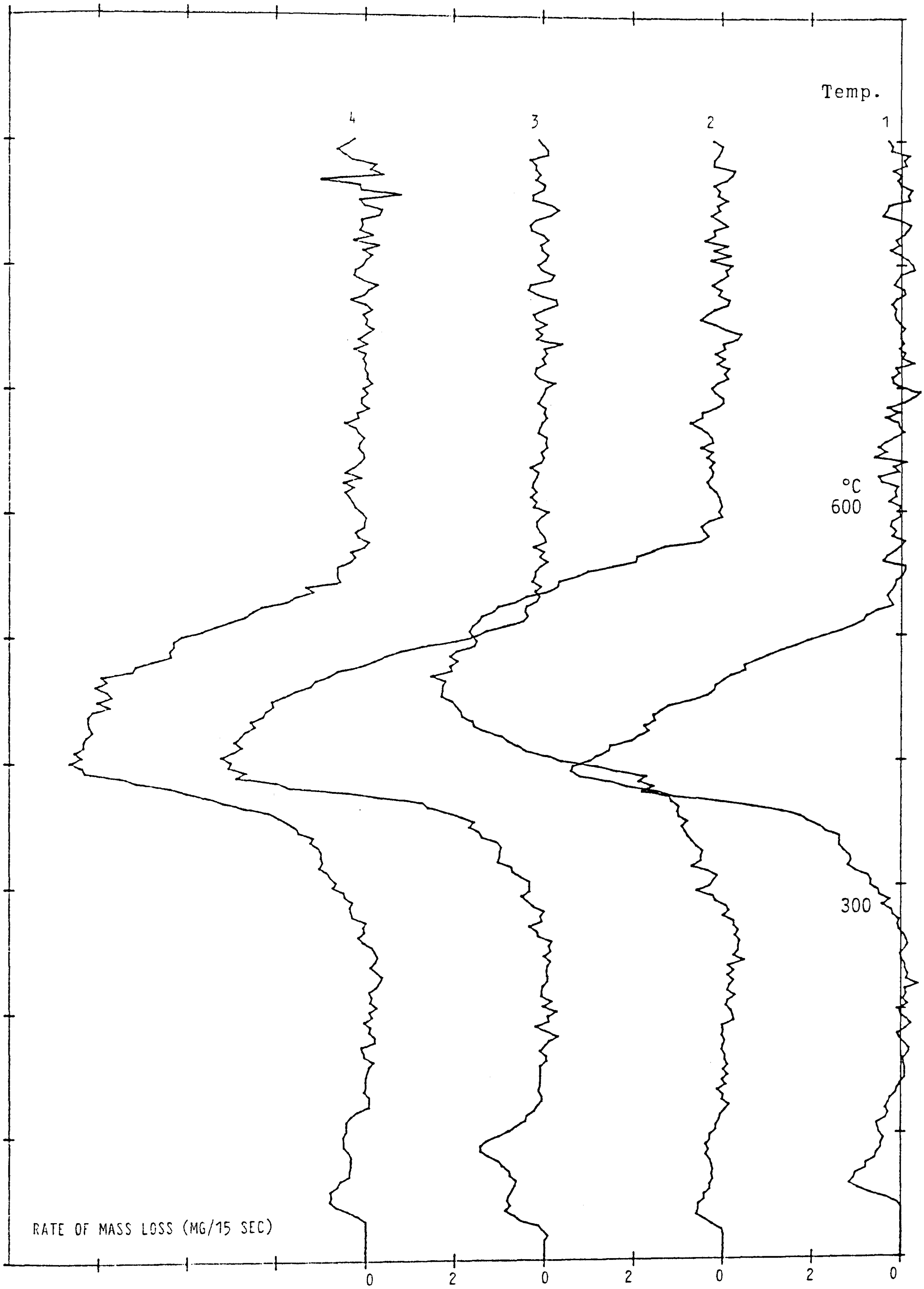


FIGURE 4.6 DTG curves for test samples

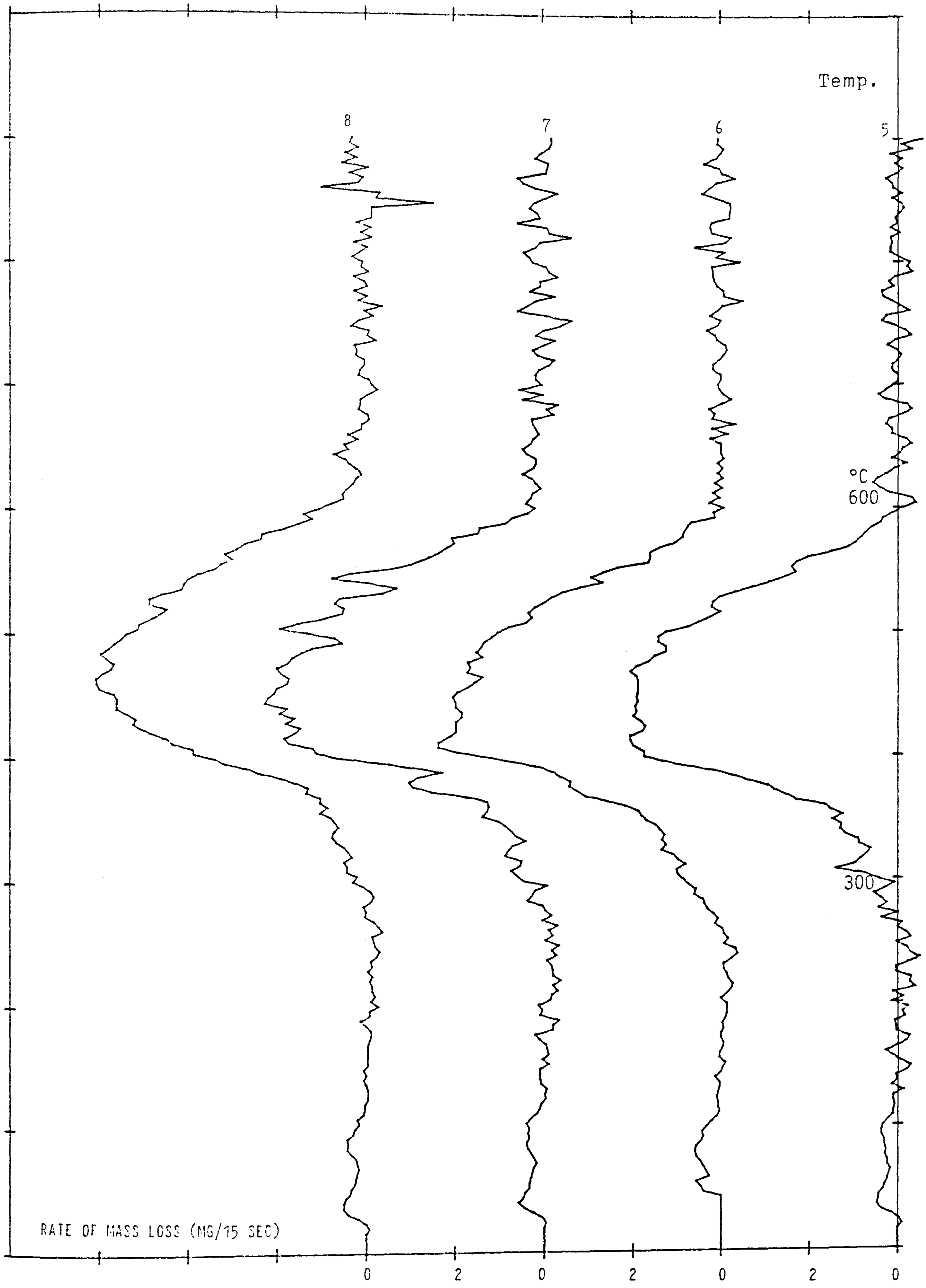


FIGURE 4.7 DTG curves for test samples

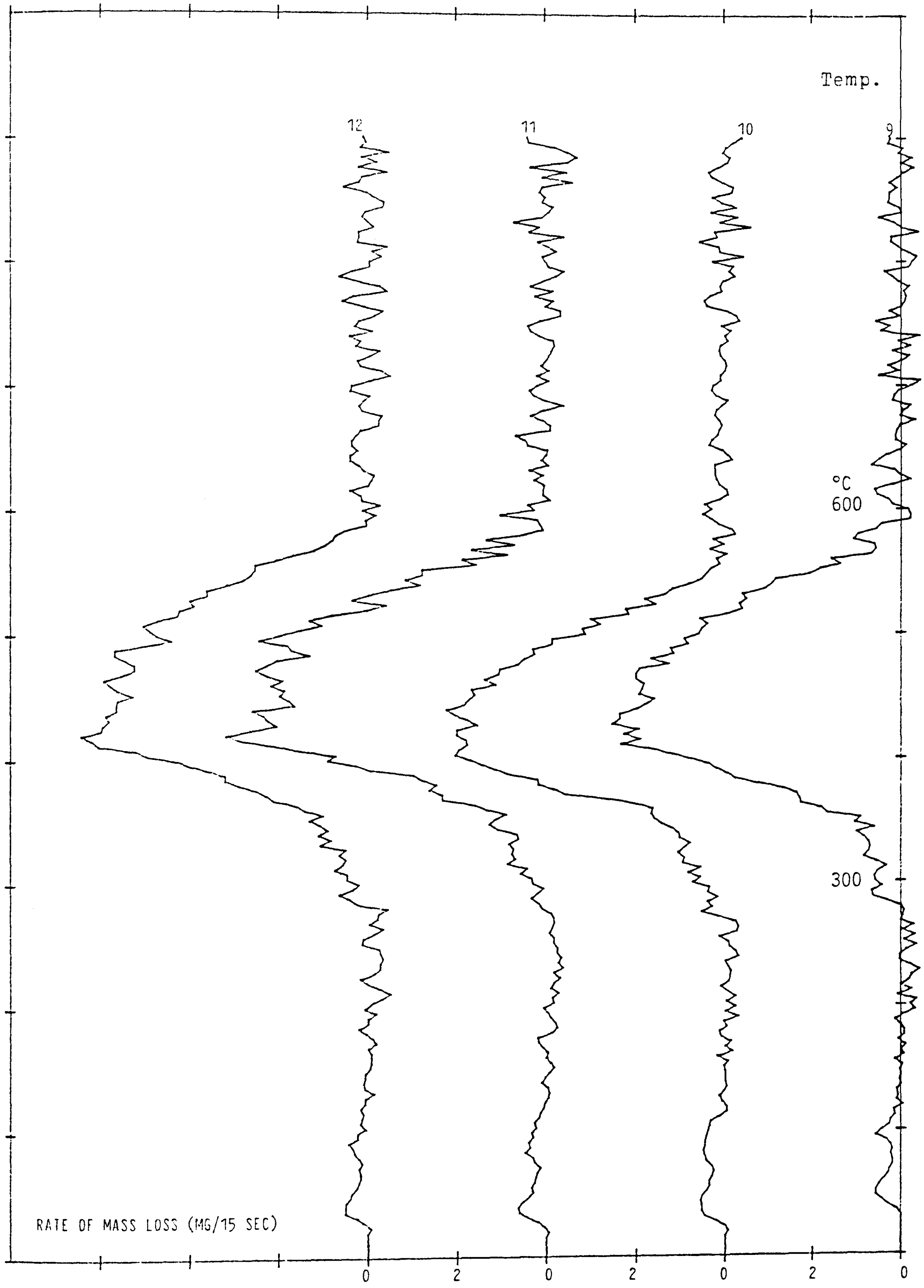


FIGURE 4.8 DTG curves for test samples

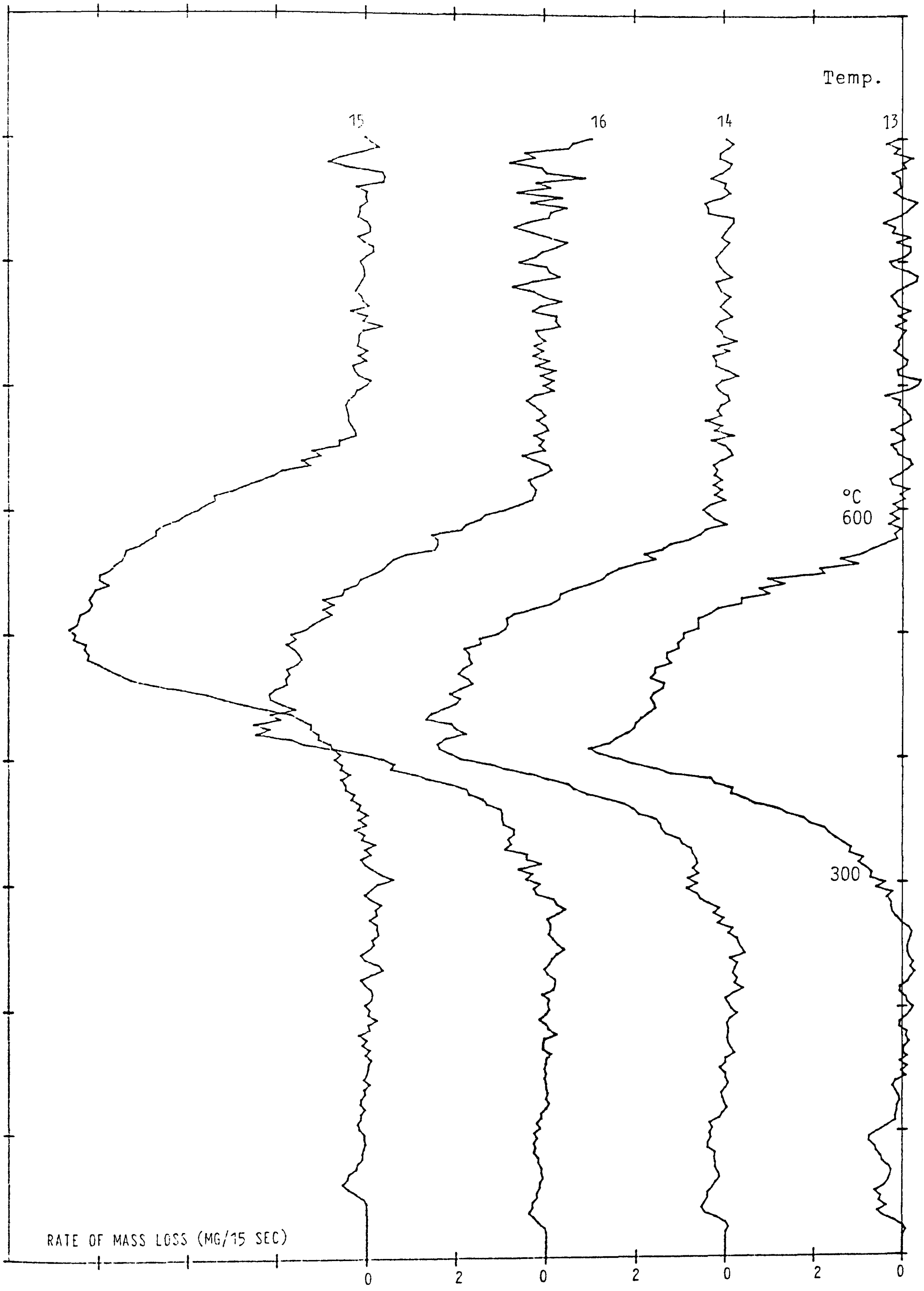


FIGURE 4.9 DTG curves for test samples

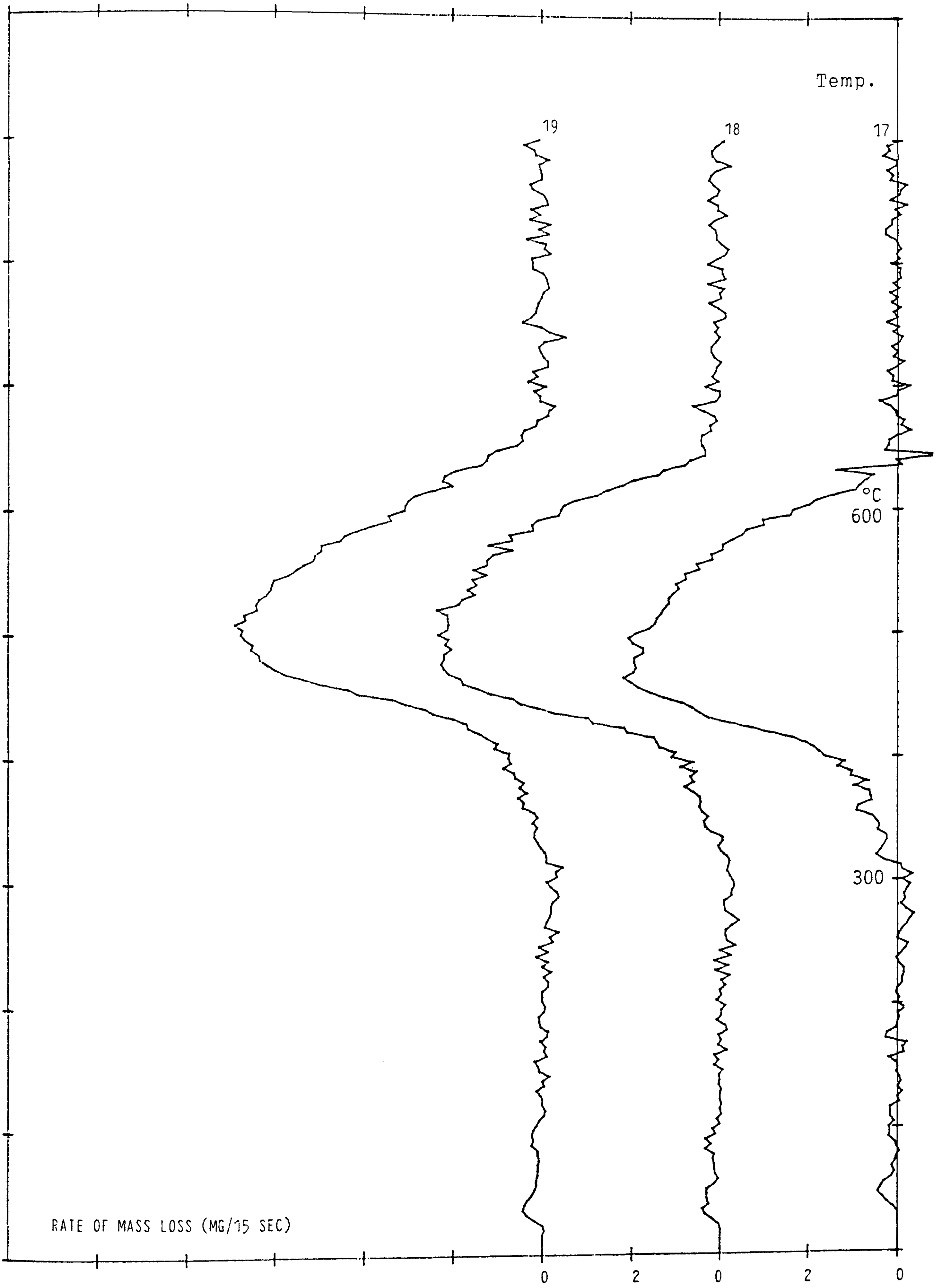


FIGURE 4.10 DTG curves for test samples

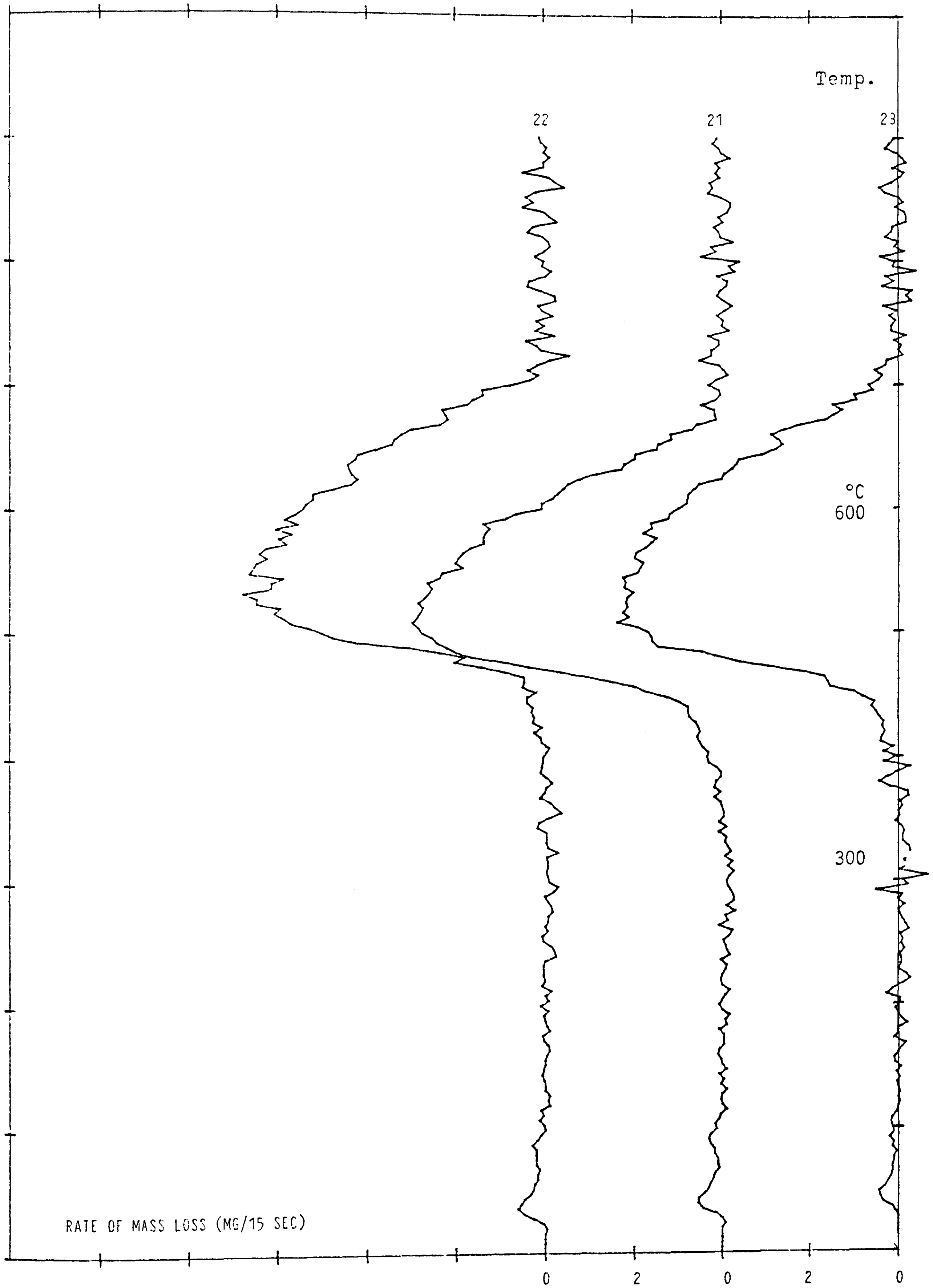


FIGURE 4.11 DTG curves for test samples

which comparisons are to be made is to determine the effects of variations in the principal classification parameters (grade/ type/rank), on some of the TG derived specification parameters. Significant changes of a TG parameter(s) along with the variation of a classification variable, will bear out how the thermal response of the coal is affected. Form variations of the DTG curves may also be diagnostic, therefore the DTG curves for the sample group under consideration are shown together.

As it was impossible to control the ash content, the fact that ash is not absolutely constant may influence the detailed patterns of behaviour of the TG curves. This aspect cannot be identified or eliminated at present, but major curve characteristics should hopefully be affected only slightly, if at all. Referring to Table 4.7 and Figure 4.12, the only justified observation is that T0 increases systematically with rank while TIC stays reasonably constant at low rank (0 - 3) levels and only increases significantly at higher (>4), ranks. A value of TIC for graphite, was determined as 800°C and T0 was 680°C. These are considered an indication of the limiting values for increase of the critical burning temperatures as a result of increase in rank. The char of high rank coals with low vitrinite content (about 30%) ignite at appreciably higher temperatures (about 460°C) than the low rank equivalents (about 420°C). The cause is not known from the TG data but is surmised to be related to the composition of the volatiles. Ash is fairly constant for all samples and therefore should have an equal, if any, effect on the ignition.

The coal for sample 19, which has the highest rank attains a higher peak burning rate than the other members of the group. It has medium reactivity (D2TGi = 6.7), and slightly lower ash but otherwise no clear indication why, at peak burning, this coal should burn faster than the others, is obvious from the considered parameters. The computed hardgrove index (HGI) of sample 19 is 60 vs. 53 for the lower ranks (Table 5.2 p 161). Sample 17 with a value of 73 burns slower, it is therefore not likely that the enhanced burning rate of sample 19 could be due to a larger fraction of fine material which is present in the sample.

TABLE 4.7

C(1,2,r).

<u>A sample group of medium grade and low vitrinite content studied for rank variations ranging from low to high.</u>

SERIES D, IE. 20-40% VITRINITE. (Refer Figure 4.12)

S #	7	8	2	17	19	
ASH	12,8	15,6	17,6	17,7	13,0	% dry
VI	32,1	26,8	21,7	33,8	33,4	% mmf
ROVmax	0,75	0,78	0,94	1,13	1,98	%
Rank	0	1	3	5	8	
T0	352	354	370	392	436	deg. C
TIC	424	402	424	446	468	deg. C
ox	3,2	3,5	5,3	4,7	4,7	mg
D2TGi	11,3	4,7	8,5	6,4	6,7	mg/min^2
Ec	22,9	23,5	31,4	26,3	24,1	kJ/mole
tb	780	780	707	810	855	s
GTR	II/D/0	III/D/1	III/D/3	III/D/5	II/D/8	(re. chem. analysis)
gtr	II/D/3	III/D/3	III/D/4	III/D/4	II/C/9	(re. TG dispersion)

ox = Adsorbed oxygen at temperatures < T0

Ec = Quasi activation parameter relating to the char fraction of the coal.

tb = Burnout time for carbon plus heavy volatiles

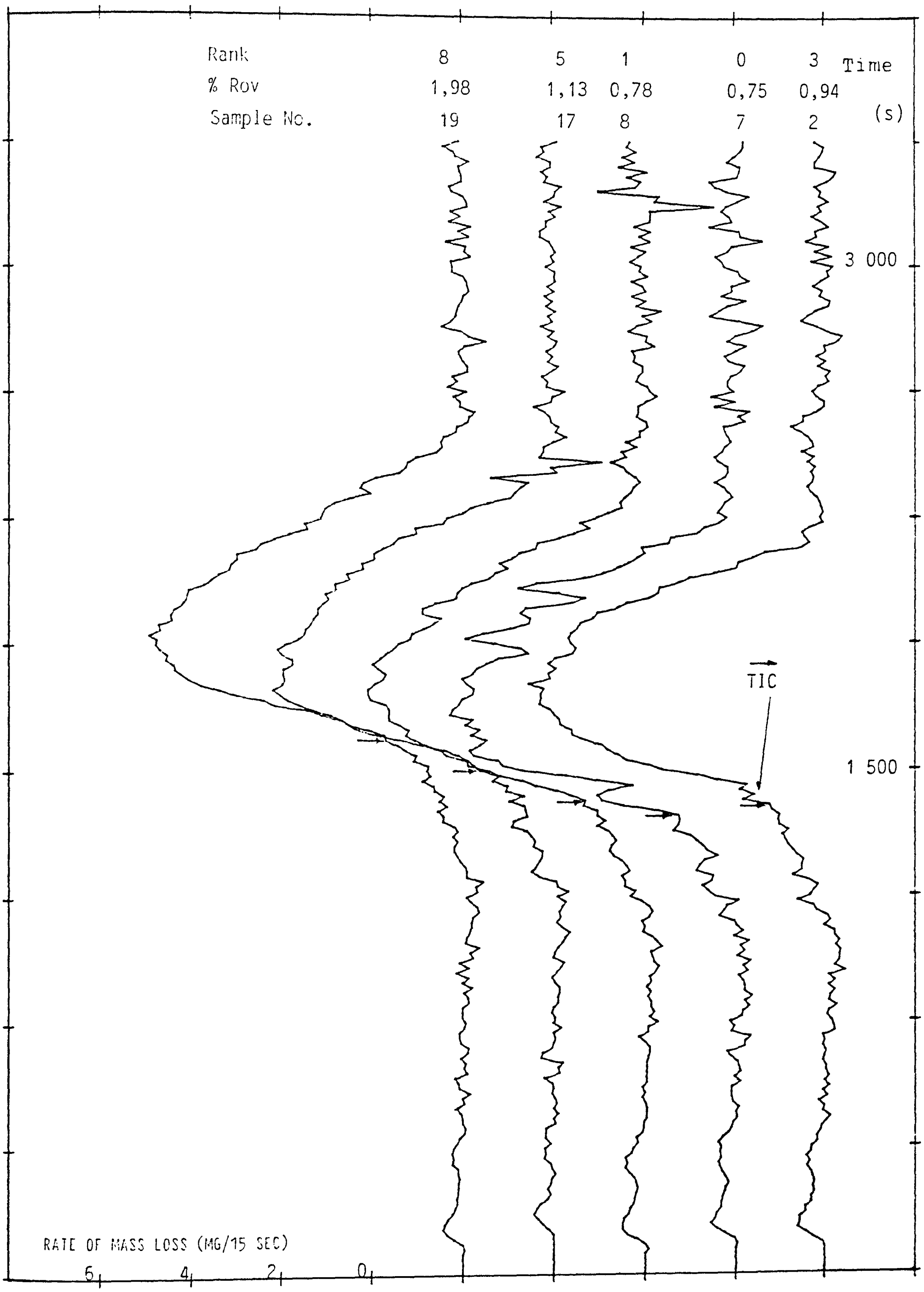


FIGURE 4.12 The effect of rank on DTG curves of sample group C(1,2,r) where r = 0,1,3,5,8

A second group of DTG curves for coals with a higher vitrinite content (about 45%) (Table 4.8 and Figure 4.13) shows no outstanding characteristics. It appears that as the rank increases only TO and TIC show distinctly upward trends. The other parameters vary stochastically which may relate to individual coal characteristics but no overall diagnostic trends are indicated.

For sample #10, the presence of high ash, (25% vs. 11% for the others) does not dampen the propensity for burning drastically: It shows the second largest D2TGi value of the group. For comparison main stage 3 of the DTG curve for pure, (97%) vitrinite (Rov = 0,.7%) is also shown in close relation to that for sample #20, with 12,.5% ash and a reactivity of 10 mg/min² (Figure 4.13). The D2TGi determined for the vitrinite (ash = 3%) is 15,.2 mg/min², and TO and TIC are 326 and 406°C, respectively. Except for the lower TO of the vitrinite the two DTG curves are very similar. The leading peak value is higher for the sample with high vitrinite content and lower rank.

Judging by comparison of the parameters at hand only the start temperature for decomposition and overall slope of the leading edge of the DTG curve appears to be affected by rank. Coal seems to part with its volatiles with greater difficulty as rank increases ie the composition of the vitrinite changes with intensified metamorphism. This could indicate that pressure and temperature effects during coalification, caused more stable chemical components to form. Barnard (1987, p 92) explains how C, H and O varies with rank. This new information yet need to be integrated with the TG results.

The upward shift in temperature for the start point of the DTG curve with increasing rank, was pointed out by Wagoner (1973, p 123). If properly calibrated, this feature, which is virtually the only clearly confirmed one by the results on Figures 4.12 and 4.13, could be used to determine the rank of coal using TG dispersion data. (The decrease of lv with increase in rank suggests that the bonds of the linking chains are altered. Refer Figure 3.13 p 50)

TABLE 4.8

C(1,3,r).

A sample group of medium grade and medium vitrinite content studied for rank variations ranging from low to high.

SERIES C IE. 40%-60% VITRINITE (Refer Figure 4.13)

S #	10	16	18	20	
ASH	25,1	11,5	11,5	12,5	% dry
VI	53,5	42,1	43,5	47,9	% mmf
ROVmax	0,65	0,85	1,94	2,75	%
Rank	0	2	8	9	
T0	324	357	422	490	deg. C
TIC	393	442	459	505	deg. C
ox	2,0	5,2	5,1	3,7	mg
D2TGi	8,8	6,2	5,9	10,0	mg/min^2
Ec	25,6	25,6	22,7	32,2	kJ/mole
tb	720	870	840	900	s
GTR	V/C/1	II/C/2	II/C/8	II/C/9	(re. chem. analysis)
gtr	V/D/3	II/D/2	II/D/8	II/D/9	(re. TG dispersion)

ox = Adsorbed oxygen at temperatures < T0

Ec = Quasi activation parameter relating to the char fraction of the coal.

tb = Burnout time for carbon plus heavy volatiles

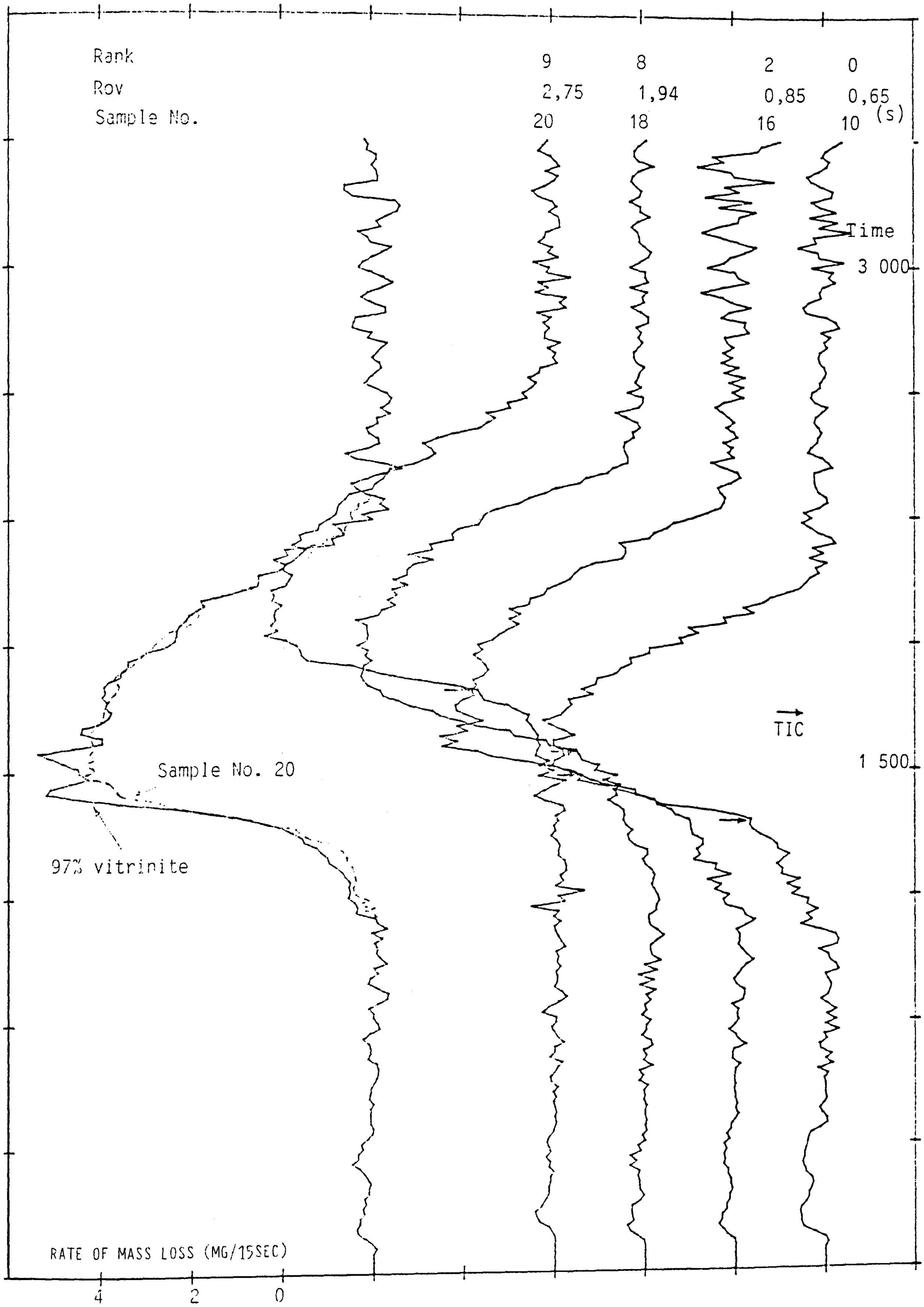


FIGURE 4.13 The effect of rank on DTG curves of sample group C(1,3,r) where r = 0,2,8,9

It is unfortunate that no comparison is possible for the lowest percentage range of vitrinite in beneficiated commercial coal products, because no samples are available (for such a study samples from the coal seam may be required). The overall picture regarding the influence of the vitrinite content, particularly in relation to rank, appears to be very mild if at all noticeable. It is rather surprising that ash does not show any prominent TG response characteristics affecting the dispersion of coal in an obvious manner. It is attempted to keep ash either low or constant but for the cases where it should obviously be the anomalous (deleterious) component, no spurious effects could so far be identified in the TG curves.

4.3.2 Influence of type variations

A diagnostic feature of the group of curves shown by Figure 4.14, is the leading peak DTG value (dotted area), which decreases with decreasing vitrinite content. The values of D2TGi (Table 4.9), however indicate that the relative "reactivity", as discussed and defined for purposes of this report (page 40), does not increase with the rise in vitrinite content but actually expands with diminishing vitrinite content. Ec values decrease while the reactive semifusinite content (RSF) distinctly rises with the increase in D2TGi values. All the other parameters such as T0, TIC etc remain reasonably constant.

This unexpected tendency in the case of low rank coals, suggests a consideration of the possible roles, in relation to the amounts in which they are present, that the other maceral groups in the samples could play: the exinite (EX), reactive semifusinite, (RSF) and inertinite (IN), percentages are shown in Table 4.9. The exinite contents for all four samples are amongst the higher percentages shown for all other samples used presently (Table 4.6). The RSF and IN percentages increase as VI decreases for the four samples (Table 4.4). If for the present it is assumed that IN remains unreactive (inert), the increased reactivity could be due to the EX together with the increase in RSF.

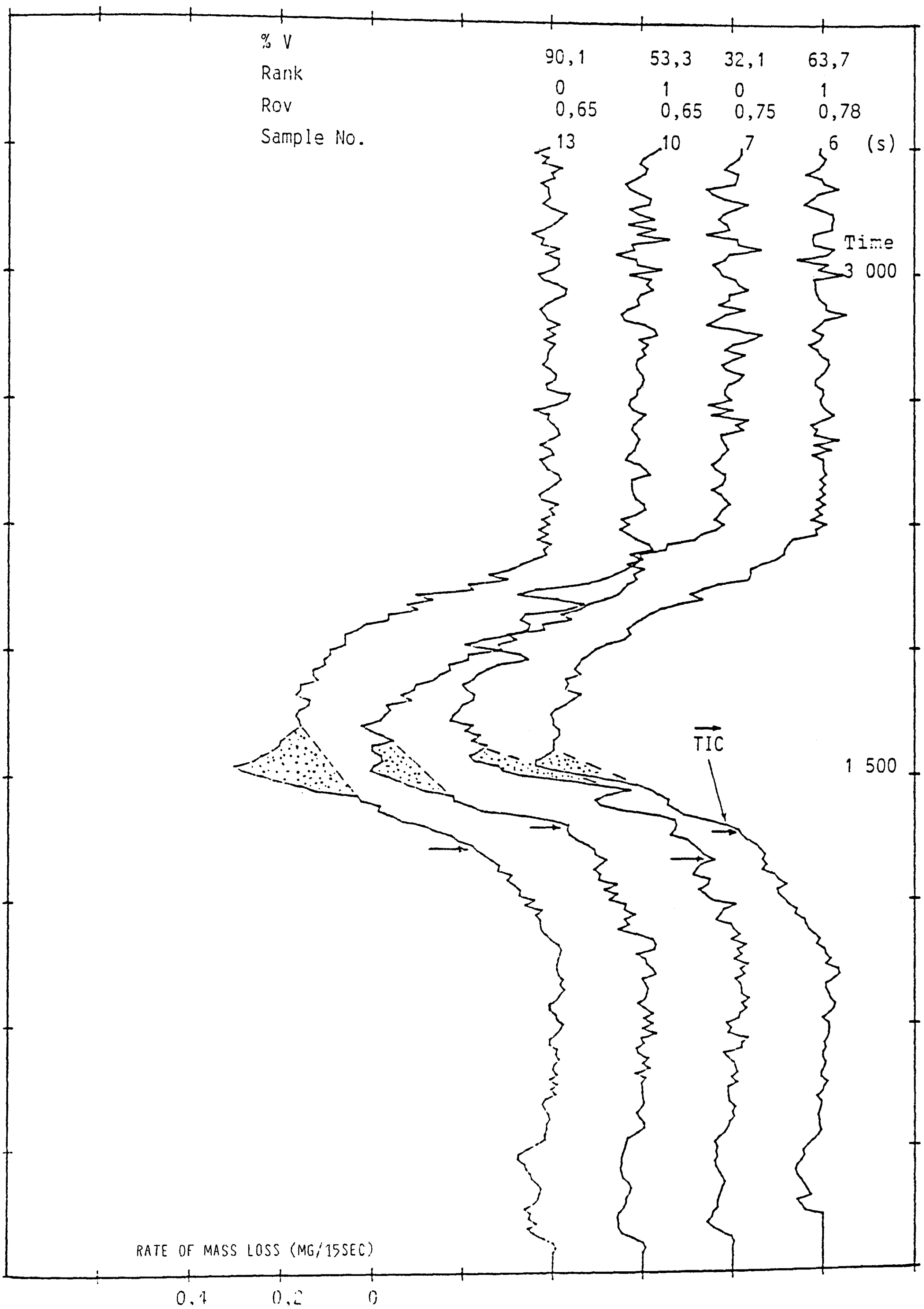


FIGURE 4.14 The effect of vitrinite % on DTG curves of sample group C(1,t,0) where t = 5,3,2,4

TABLE 4.9

C(1,t,0).

DTG curves for zero rank with variation of vitrinite content from type A to D.

TYPE VARIATIONS AT RANK ZERO LEVEL (Refer Figure 4.14)

S #	13	6	10	7	
ASH	10,2	12,1	25,1	12,8	% dry
VI	90,1	63,7	53,5	32,1	% mmf
EX	5,0	8,0	6,5	7,0	% mmf
RSF	1,5	7,6	10,7	21,4	% mmf
IN	3,4	20,5	29,3	39,3	% mmf
ROVmax	0,65	0,78	0,65	0,75	%
Type	A (90%)	B (70%)	C (50%)	D (30%)	ave.%
T0	324	324	324	352	degr. C
TIC	415	424	393	425	degr. C
ox	2,5	3,2	2,0	3,2	mg
D2TGi	5,2	5,6	8,8	11,3	mg/min^2
Ec	30,1	29,0	25,6	22,9	kJ/mole
tb	870	765	720	780	s
GTR	II/A/0	II/B/1	V/C/1	II/D/0	
gtr	II/B/2	II/D/3	V/D/3	II/D/3	

ox = Adsorbed oxygen at temperatures < T0

Ec = Quasi-activation parameter relating to the char fraction of the coal.

tb = Burnout time for carbon plus heavy volatiles

The bulk of this information suggests that the relatively high level of EX together with the increase in RSF combines to sustain, and even increase, the reactivity of the coal although the vitrinite content is lowered (although important, vitrinite alone does not seem to control propensity for burning). The results of a TG dispersion test on samples of torbanite (rich in exinite 95%), vitrinite (97%) and inertinite (88%), are shown in Figure 4.15. The reactivities for these samples, expressed as D2TGi values, are 186, 15,8 and 7,8 (mg/min^2) respectively. The importance of even small amounts of exinite in a sample is therefore indicated.

The relation between the DTG and D2TG curves for the three maceral groups is also shown. From the correspondence between the peak c (Figure 4.15) on the vitrinite curve, and the centre peak C of the exinite curve, (inertinite shows none), it is most likely that, either vitrinite and exinite have a common response peak around 425°C, or that the vitrinite may contain a small percentage of exinite, the response of which is superimposed on the overall vitrinite curve. The latter would mean that the DTG curve for any coal should represent the integrated effect of the macerals within it. This seems to be borne out by the weak vitrinite peaks, marked a, d and e, which can also be correlated with peaks on the exinite curve, marked A, D and E. The DTG curves have been smoothed very slightly so that some risk exists that misleading noise peaks could lead to spurious correlations.

The leading peak on the vitrinite curve b, has no equivalent in any of the others and inertinite shows only a possibility that peak Ex, may correlate with e, and E. The shift in peaks is important because distinct sequences of peaks are notable in the DTG curves of certain coals which make it difficult to determine TIC. It seems that different ignition temperatures could be present in the same sample eg Figure 4.12 number 7. The low slopes on the waxing edge of the inertinite (Figure 4.15) shows that it has a low propensity for burning.

The D2TGi values on the D2TG curves, which are plotted on the same scale, show that torbanite, most probably as a result of the

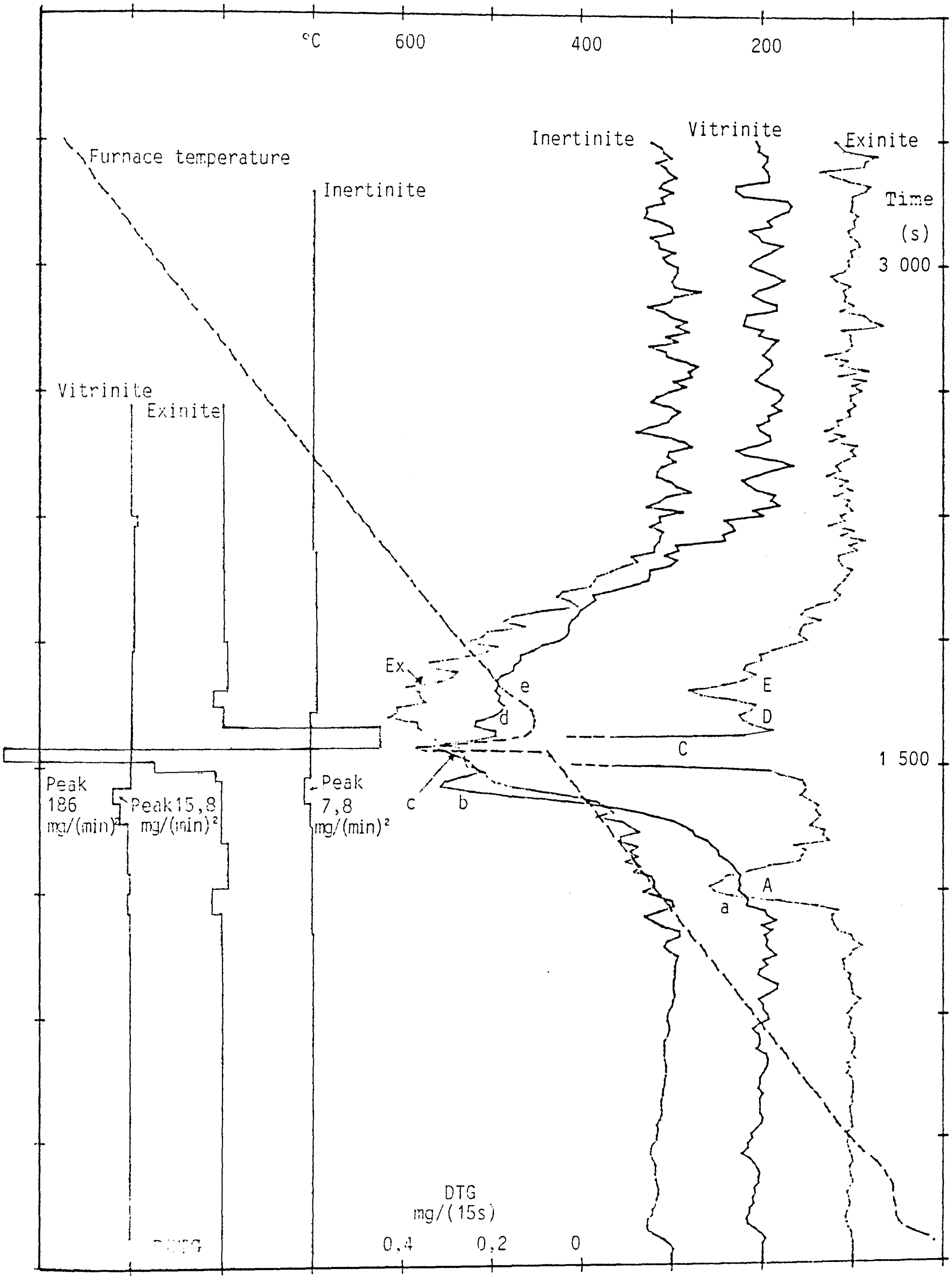


FIGURE 4.15 Compring TG responses of exinite (torbanite), vitrinite and inertinite

presence of exinite, is about twelve times more reactive than vitrinite. That intense heat is released is shown by the temperature peak superimposed on the furnace temperature (dashed curve).

This temperature increase of about 100°C, does not represent the normal near sample temperature (QDTA) value. It is the temperature recorded by the furnace control thermocouple which is about 10 mm below the sample container. The flame temperature at ignition must be in the order of 1000°C, which is much higher than usually recorded for coal.

Since only one set of test specimens is presently available this very significant finding cannot be elaborated upon without further investigations: a matter which is receiving attention. In general it appears feasible that vitrinite contributes towards the generation of light volatiles ie it enhances inflammability. Vitrinite in conjunction with reactive semifusinite ensure conflagration after ignition and these two maceral groups together with exinite cause deflagration. Inertinite is a burnable substance, but lacks propensity for burning and requires substantial support from the other macerals before it will burn without defaulting.

4.3.3 Influence of ash variations

In Figure 4.16 none of the specification parameters shows definite trends which can be linked with ash content. The curve forms are very similar, all showing the vitrinite peaks which are characteristic of low rank coals. Very similar peak burning rates are shown, and burn out times (Table 4.10) are in accordance with the ash content ie the highest ash has the shortest tb. The ignition temperatures are reasonably in agreement but that of the higher ash coal (25.1%) is the lowest.

The second group of DTG curves for which ash is the principle variable is shown in Figure 4.17 and Table 4.11. In this case TO values are reasonably close but TIC values again show that the coal with the highest ash value not only ignites at the lowest temperature (385°C) but is also the most reactive with a D2TGi

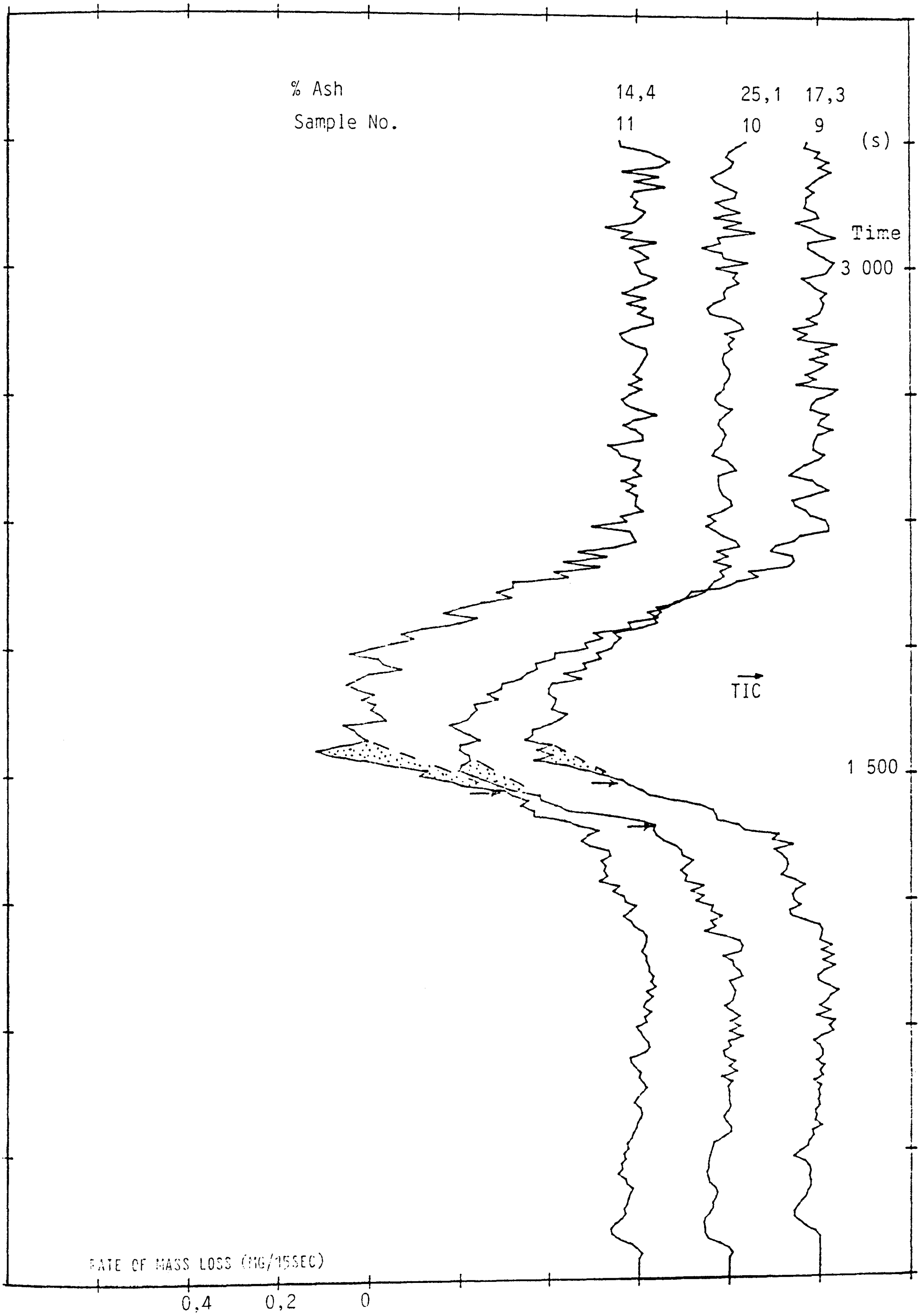


FIGURE 4.16 The effect of ash % on the DTG curves of sample group C(g,3,0) where g = 1, . . .

TABLE 4.10

C(g,3,0).

__Variation in the DTG curves for coals which have the same rank and type but for which the ash contents vary__

TYPE C AND RANK ZERO (Refer Figure 4.16)

S #	10	9	11	
ASH	25,1%	17,3%	14,4%	% dry
VI	53,5	48,1	41,6	% mmf
ROVmax	0,65	0,68	0,74	%
T0	324	325	357	deg. C
TIC	393	424	407	deg. C
ox	2,0	3,9	3,7	mg
D2TGi	8,8	6,3	7,7	mg/min^2
Ec	25,6	29,3	27,4	kJ/mole
tb	720	735	765	s
GTR	V/C/1	III/C/1	II/C/0	
gtr	V/D/3	III/D/3	II/E/4	

ox = Adsorbed oxygen at temperatures < T0

Ec = Quasi activation parameter relating to the char fraction of the coal.

tb = Burnout time for carbon plus heavy volatiles

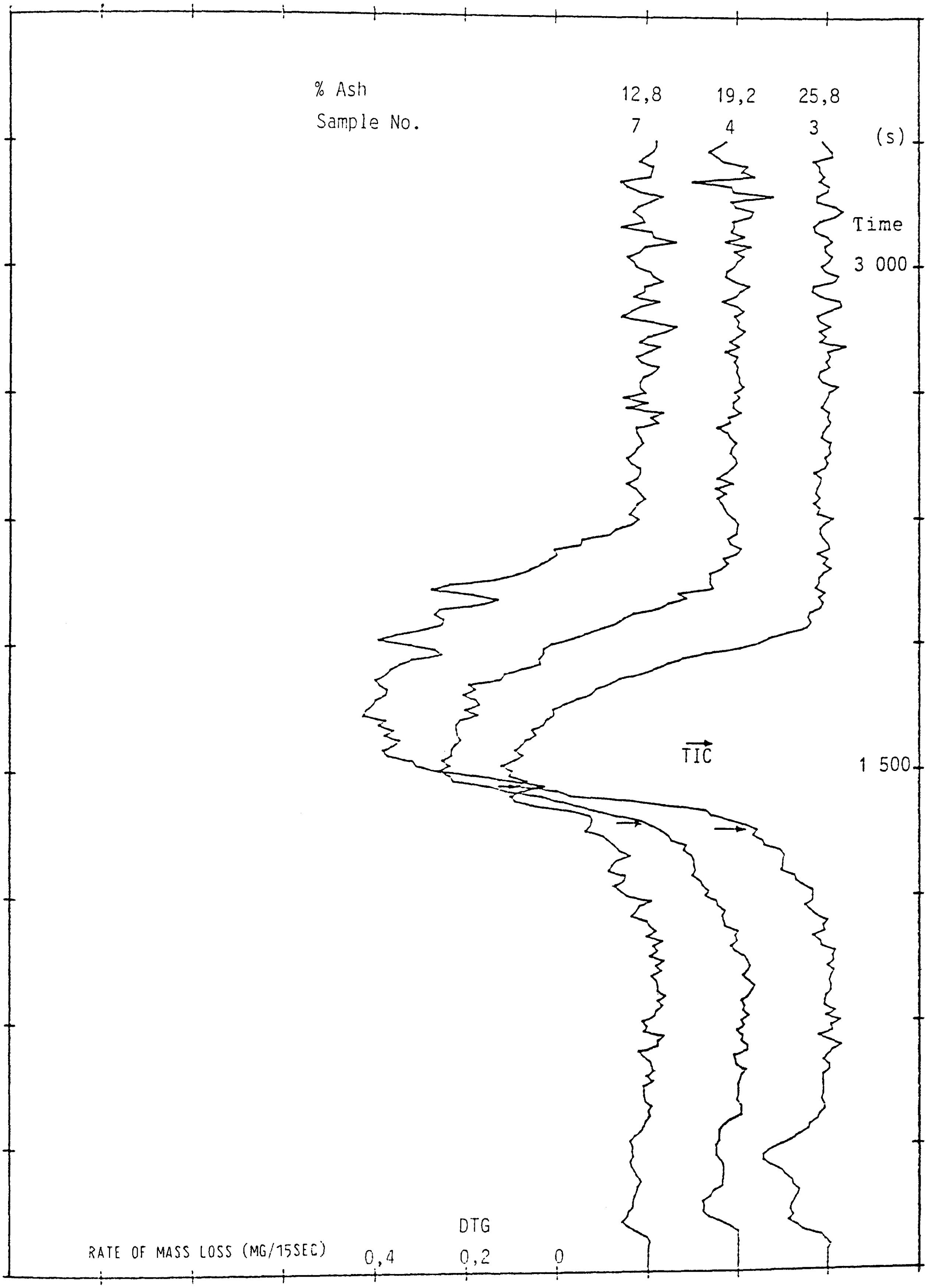


FIGURE 4.17 The effect of ash % on the DTG curves of sample group C(g,2,0) where g = 1,2,3

TABLE 4.11

C(g,2,0).

<u>Variation in the DTG curves for coals which have the same rank and type but for which theash contents vary</u>

TYPE D AND RANK ZERO (Refer Figure 4.17)

S #	3	4	7	
ASH	25,8%	19,2%	12,8	% dry
VI	30,6	40,9	32,1	% mmf
ROVmax	0,74	0,67	0,75	%
T0	340	341	352	deg. C
TIC	385	389	424	deg. C
ox	1,0	3,3	3,2	mg
D2TGi	15,8	8,0	11,3	mg/min^2
Ec	32,0	25,3	22,9	kJ/mole
tb	600	720	780	s
TGR	V/D/0	III/C/0	II/D/0	
tgr	V/D/3	III/D/3	II/D/3	

ox = Adsorbed oxygen at temperatures < T0

Ec = Quasi activation parameter relating to the char fraction of the coal.

tb = Burnout time for carbon plus heavy volatiles

value of 15,8 mg/min². It has the shortest burn out time, low vitrinite content, medium RSF, and highest Ec.

The observation that for the two different sample sets (Figures 4.16 and 4.17) high ash samples apparently ignite at lower temperatures and are more reactive than other coals with appreciably less ash, is unlikely to be fortuitous. As all the coals which are represented by the samples are commercial products which are consumed by users as good burning coals, there is no doubt about this aspect. It is however not clear how ash could enhance burning. A possible explanation may be that mineral matter could enhance the microporosity of the char formed by devolatilisation of the coal and that this increased porosity has a beneficial effect on reactivity. Ash is therefore a deleterious component of coal as far as economics and bulk heat supply is concerned but it need not necessarily be harmful to the burning process.

The overall pattern regarding the role of ash in burning appears to be not very accentuated; otherwise it should have been more conspicuously apparent from the DTG curves. The implications of this preliminary interpretation are important because it means that high ash coals may be readily burnable and can be used for heat generation, as is being done by ESKOM.

4.3.4. Devolatilization Phenomena

Volatile matter which is expelled form coal as a result of heating must originate from the macerals as well as certain inorganic compounds. The effluents which emerge as oxidation products from burning of coal mostly consist of carbon dioxide and water vapour which provide no indication of the original sources. From the analysis of effluent products the total heat which is generated can be computed but the effluents provide little information regarding **the manner in which the maceral components of coal contribute towards the generation of heat.** If the decomposition products are to be analysed oxygen must be excluded as an external reactant to avoid burning.

The states S(i,1,k), where i < 4 and k =/= 2, or =/= 5, (Figure 3.2 p 21), provides for a series of experiments where the manner in which volatiles are released from coal during heating, can be observed (=/= not equal to). Unless special additional provisions are made for continuous analysis, the composition of the volatiles which are liberated at specific temperatures remains unknown. However stages of either drastic mass variations or stable states will at least reveal where major decomposition occurs for different coals. If these temperatures are correlated which characteristic features of classified coals the order in which macerals decompose may be determined empirically. It is even possible that the overall devolatilisation curve may reveal information which could assist further to facilitate a better understanding of the thermal response of coal.

Extensive devolatilization tests have not been executed with the equipment at hand but the information presented in Figures 4.18 and 4.19 may provide insight into the type of applications which are possible. These figures represent data for a vitrinite concentrate of a low rank bituminous coal, represented by the 1.32-1.34 RD fraction (Moodie 1977, p 22).

The results of four tests are presented, TG dispersion S(1,1,1) in Figure 4.18 and drop furnace tests with air excluded S(3,1,1) and in atmospheres of, nitrogen S(3,1,3) and carbon dioxide S(3,1,4) are presented in Figure 4.19. The sample was contained in a shallow solid pan with a lid.

For the dispersion devolatilization (Figure 4.18) it can be seen from the QDTA curve that although the major process is endothermic there are two sections when, exothermic reactions occur. The mass loss curve is recorded for the sample in the weighing pan with lid on but air on the outside ie the reactants are in equilibrium with the products. It was expected that exponential response curves would be common for this test but the results show that initially gas, and water are released and thereafter, much like for a standard dispersion, the DTG curve shows various substages during which specific disintegrations of the coal components occur. These are marked (but not numbered) for the various curve stretches of the DTG curve and projected to the other related curves (a temperature range and mass fraction can

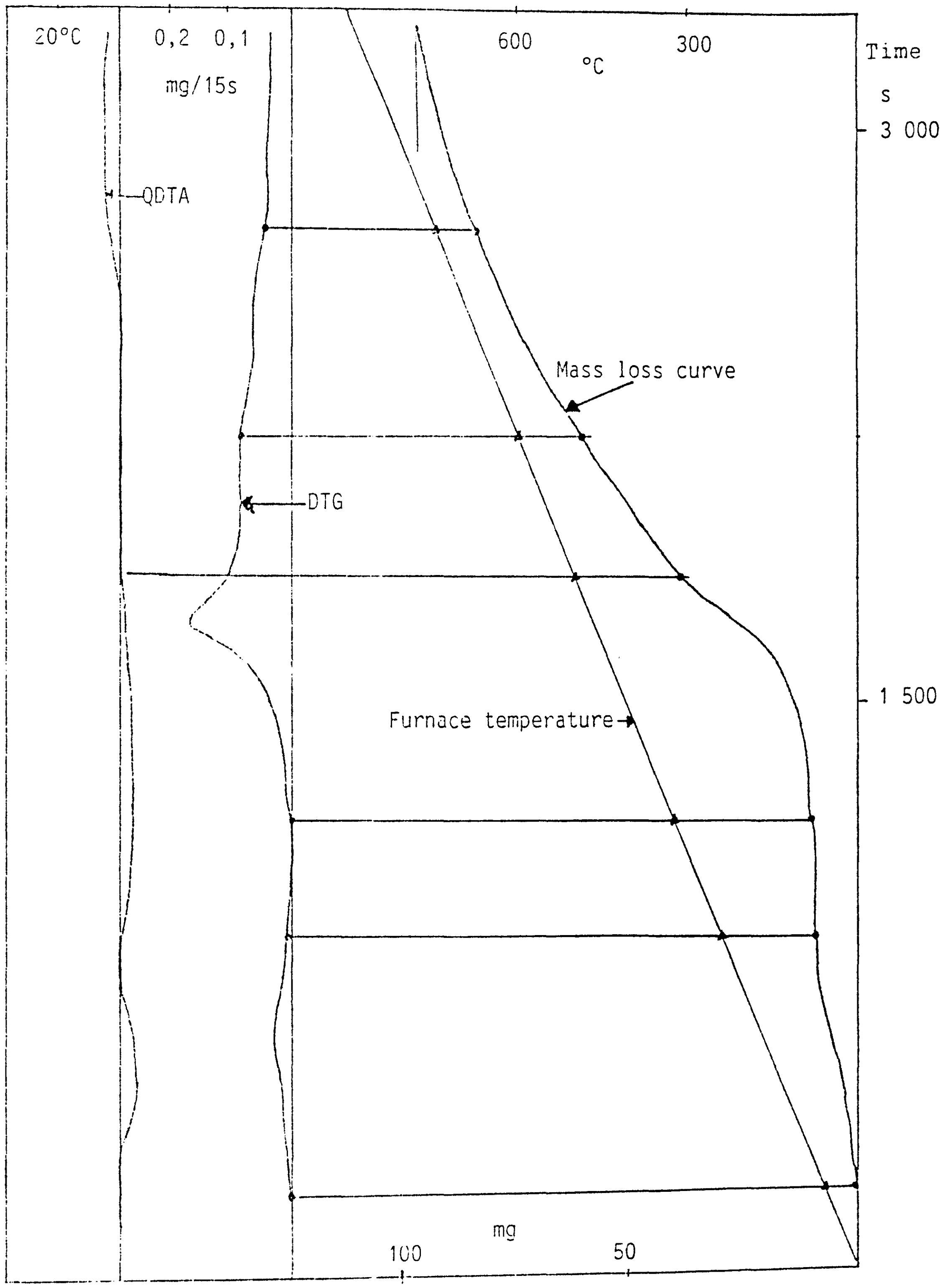


FIGURE 4.18 Dispersion devolatilization of vitrinite concentrate

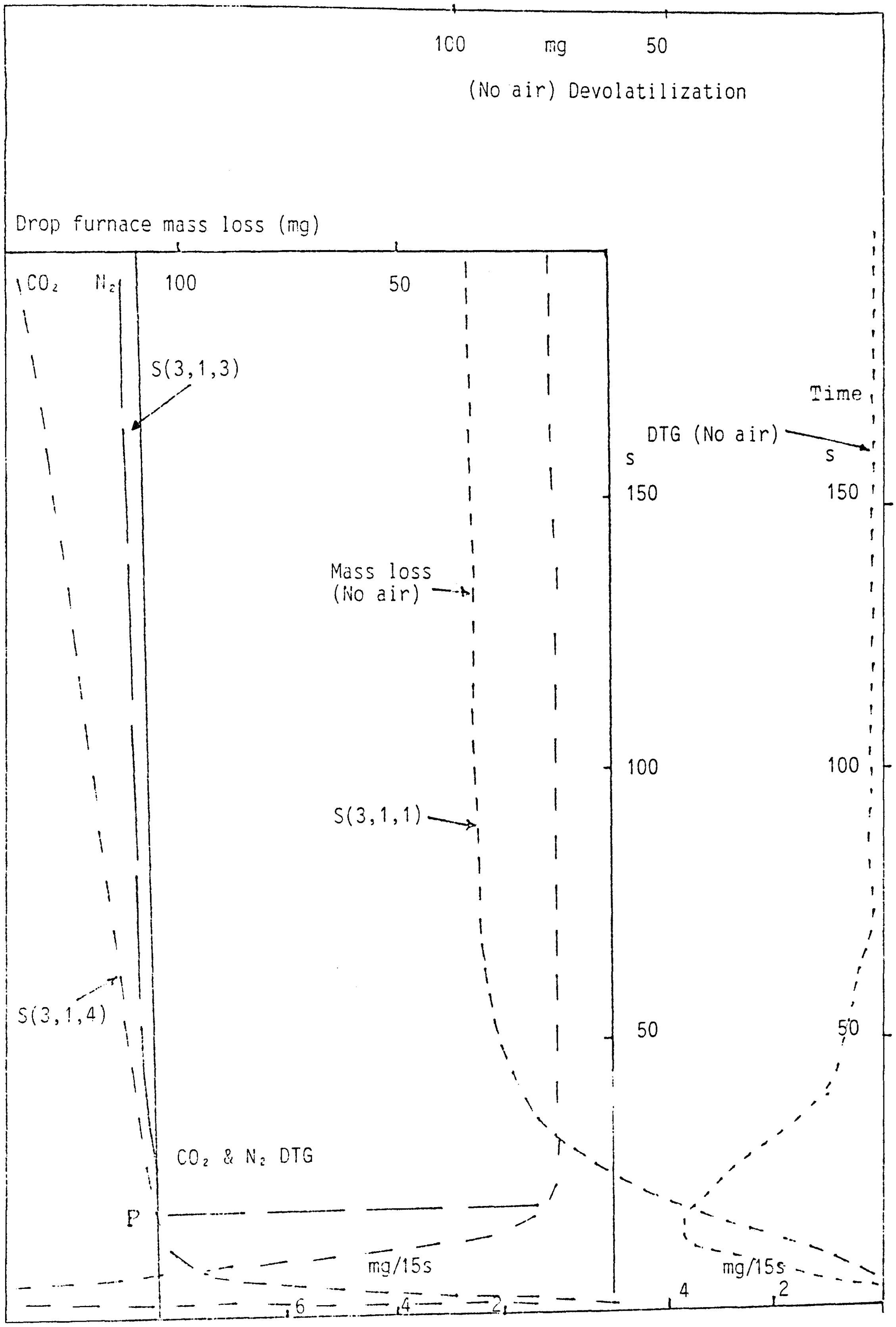


FIGURE 4.19 Drop furnace devolatilization of vitrinite concentrate

be identified). The end value of the mass loss curve shows the total volatiles which are released.

The exothermic and endothermic reactions are unidentified at present. If the volatile compositions are monitored continuously, a distribution pattern can be established similar to that derived from Juntgen _et al_'s data (1979) and shown in Figure 3.14.

When the sample in the container with the lid on, is subjected suddenly to a temperature of 1000°C, S(3,1,1), the results (short dashes), along with other data for comparison, are shown in Figure 4.19.

The drop devolatilisation test, S(3,1,1) shows a mass loss curve which is of shorter duration than that from the dispersion test: It resembles the way in which volatiles are liberated during burning. After the volatiles are released the mass stays virtually constant, The very slight loss is probably due to the infiltration of air which causes oxidation. The final loss of volatiles, vm, matches that of the dispersion technique and the proximate value VM, very well.

For the cases where the sample was suddenly exposed to high temperature, but in an open container, S(3,1,3) and S(3,1,4) ie in the presence of nitrogen and carbon dioxide respectively, the long dashed curves were obtained (Figure 4.19).

The initial sections of these latter two devolatilization tests are so similar that only one medium dashed curve is shown to present the data from start to point P. Only from P towards the end does the carbon dioxide medium start to react differently.

The nitrogen assumed essentially a stable state but the carbon dioxide reacted with the carbon in the pan presumably to form carbon monoxide with the result that a linear rate of mass loss is attained.

The reactivity of the char with respect to carbon dioxide can be calculated. For the specific conditions a value of 8,6 mg char/min is transformed to carbon monoxide. This measurable parameter could be useful in connection with the TG properties of coke.

4.3.5 Granularity

Most humic coals are layered. When the coal is broken down the smaller the lumps become the more will the coal represent a statistical distribution, not only of granule sizes, but also of dark and bright particles. Raab (1974) studied the habit of grain size distribution of several South African coals and found that, (op cit p 9), "It became evident that the size distribution of run-of-mine coal for all collieries was almost the same. They differed only in the coarseness or fineness of the products. The investigation proved that the mining method (drilling, cutting, blasting) does not alter the size distribution".

To test the consistency of size distribution of samples processed by standard techniques for laboratory analysis the size distribution of three -70 mesh samples from the same mines studied by Raab was determined. The size distributions corresponded well with the patterns determined by Raab. It thus appears that coal from a given mine maintains reasonably fixed proportions of particle sizes within specific ranges. From a TG point of view this means that coals can be compared arbitrarily, also for ranges smaller than 0,21 mm diameter. Where burning of coal is concerned, the ratio of the different lithotypes, vitrain, fusain, clarain and durain, within the set size distribution remains an unknown factor.

Moodie (1977) studied maceral distributions in the Witbank No 2 Seam. One of his conclusions which may influence the interpretation of TG results is that peas contain a slightly higher amount of vitrinite which tends to concentrate in the 1,35 relative density float material (op cit p 22). It should therefore be possible to acquire coal in which vitrinite should predominate.

To accommodate granularity in an organized manner, a distinction is made outside the S(x,y,z) matrix, ie for each grain size group the complete experimental state-matrix is applied. TG effects of specific coals are dealt with through the C(g,t,r) matrix which is applied to classify the coal.

Table 4.12 shows how the TG equipment is adapted to deal with grain size variations used on grate type burners as well as in pulverized fuel furnaces.

For dispersion analysis the complete range of grains, formed naturally during grinding to -70 mesh, is used in the sample. It is attempted to minimize the effects of granularity by directing the flame front to migrate downwards through two to three layers of evenly spread granules of coal, with oxygen supplied essentially from the top. The mass flow emerges upwards, roughly as a "plane" front with reasonably equal density. Tests with various fractions of selected grain sizes show that repeated results of the dispersion test do not vary significantly as a consequence of limited variation in grain size distribution. The repeatability of a TG test was pointed out by Wagoner et al (1973, p 122).

In the drop furnace technique where the actual burn out parameters are important, the sample size is reduced and the grains, sometimes sized to smaller ranges as indicated by the crosses (Table 4.12). The sample is spread out as a single layer on a fine mesh container. The air which is passed upwards and across the sample, has access to all sides of each grain with the result that inward moving flame fronts are set up, with air reaching it from all sides. This enables true grain burn out times to be established: for each sample of granules (assuming identical composition), set up in this fashion, only the largest particles will determine the total burn out time.

By using a burn out function for the particular coal under consideration, such as eg $tb = C.d^2$, derived by Essenhigh (1963, p 185), and the appropriate grain distribution function, as described by Raab (1974), the burn out profile for the sample of pseudochar can be simulated on a computer and expressed as a computed mass loss curve (d=particle diameter, C=const). Using tm, the burn out time for the largest particle, with diameter dm, a value for C can be determined.

TABLE 4.12

Normal grain sizes for TG processing.

```
                  |                                    |
******** Smalls **>|<************ Duff*****************|<*PF*>
-----------------------------------------------------------------
Grain mm:   10     5    2.5   1.0    0.5   0.25  .125   .07 <0.07
-----------------------------------------------------------------
            |      |     .     .      .     .  |   .    |   |
            |      |                           |            |
Grid Flash: |(Non TG: not dealt with presently)             x--->
            |      |                           |
            |      |     .     .      .     .  |   .    |
            |      |                           |
Dispersion &|Devolatilatilization      [a]     x-(standard)----->
            |      |                           |        |
       [b]  x---(special studies)---------->   |        |
            |      |                           |        |
Drop Furnace|[a] <-x-><--x-><-x--><-x--><-x--><-x--><-x------>
            |      |                           |        |
            |[b]   |                           x---------------->
            |      |                           |        |
            |      |     .     .      .     .      .    |
            |
  <--------x|(>10 mm Not studied but TG application possible)
```

[a] = the standard range of grain sizes used

[b] = an alternate range of grain groupings which is also used

Note it is attempted to use the total range of grain sizes which occur in the commercial products Smalls to Duff coal.

This provides an analytical basis for the derivation of mass loss curves using experimentally determined parameters. A problem associated with this approach is that the assumption of spherical particles does not apply to coal unless it is in a very fine state. Despite this shortcoming the behavioural trends of particles can be determined under simulated conditions where only one variable can be introduced for studying. The objective is to establish in what manner the mass loss curve is influenced by various factors so that these could be looked for in practice.

Figure 4.20 shows the results of simulated TG curves for char where the grain size distributions are shown schematically in relation to an actual distribution. The determined distribution is shown by the bar diagram, and curve (A) is the computed mass loss curve based on this grain size distribution, using an observed burn out time and a 0,21mm max. grain size. The algorithm for the computation of the cumulative mass loss as a result of burn out of the assembly of particles, assuming overall simultaneous ignition, is based on Essenhigh's burning law. (1983, p 185)

Curve (B) shows the simulated curve when a normal distribution of grain sizes around the mean, illustrated schematically by the solid curve envelope, is assumed. The close correspondence with curve (A), which is close to a normal distribution is obvious. When the size distribution is skew towards the smaller diameters, as illustrated schematically by envelope (c), the corresponding ML curve is shown by curve (C). It can be seen that the burn out time is reduced appreciably when compared to the case for grain size shifted to the coarse end. The latter is demonstrated by envelope (d) and ML curve (D) respectively.

An important point is illustrated by the steepening of the ML curve as a result of faster burn out due to smaller grains: This steepening will increase the value of D2TGi, which means that an increased apparent "reactivity" can result from reduction of the particle sizes in a test sample. This aspect must be considered when reactivities are interpreted ie only samples of reasonably similar grain distributions must be compared.

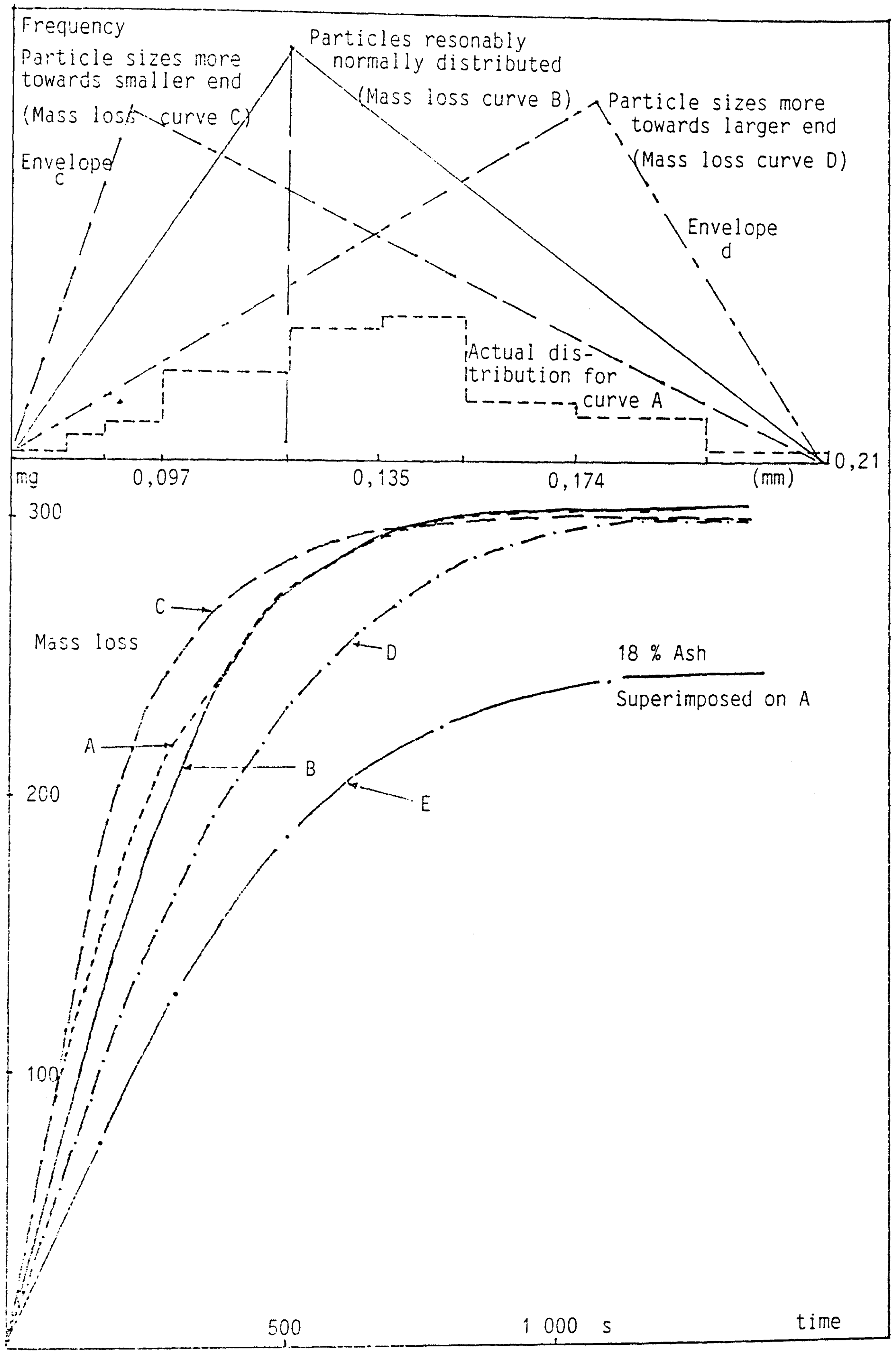


FIGURE 4.20 Computer simulation of burning different sizes of coal particles

A comparison between the emulated burning profile obtained from actual burning of a sample in a furnace, and the simulated TG curve, in principle can provide useful information concerning synthesis of the burning process: Curve (E) shows the curve which should result when 18% of the sample is retained as ash which is formed linearly over the sustained burn out time. Under these conditions ash should reduce the value of D2TGi.

Burn out times for individual very fine, ie< -,050 mm particles under practical conditions, cannot be dealt with effectively using TG techniques because the smaller the particles get the smaller the burn out times become. The normal scale is limited to a reading response time of one second, and faster reading rates cannot be measured, using TG equipment. For the PF particle range the rate of formation of the reaction products, ie the right side of R1.1, must therefore be measured instead. These tests are usually referred to as **Grid Flash or Drop Tube Furnace** techniques which are not dealt with here. These techniques are however not too far removed from TG techniques and, on account of the fair amount of common features, cannot be separated entirely from TG procedures.

5 PRACTICAL THERMAL ANALYSIS OF COAL

Various elements were discussed which involve the interpretation of data concerning the response of coal to heat. Finally these components need to be integrated to produce useful information regarding how the coal is expected to burn.

If burning could be considered a single chemical reaction the normal theory involving the appropriate rate constant and activation energy would be sufficient for comparing all fuels. Studies by various authorities, Daniels (1972), Unsworth (1986), as well as the present analysis, have shown that due to the complex nature of the flame front the mass loss which is measured by TG tests cannot be interpreted stoichiometrically; frequently other empirical approaches are more suitable.

Essenhigh (1955) pointed out that burning of coal involves two fundamental components namely combustion of volatiles and burning of char. These two components can be interlinked in various ways in which certain processes dominate. Essenhigh (1970, p 1) pointed out that it is difficult to design experiments which can bear out relevant information about the dominant complex reactions unambiguously. The best that can frequently be done is to derive pointers which indicate that specific scientific surmises are likely to be correct: deduction of the burning behaviour of coal is a piecemeal process of fitting together bits of relevant information which were observed, frequently not even in the same experiment. This collation of information requires scientific expertise and cannot be routinised because of the varied nature of the assessments which are required. For the present an evaluation of the overall results from the group of coals is presented.

The information in part consists of the normal proximate and ultimate analysis values supplemented by detail furnished by TG analysis. There are also derived maceral contents (vitrinite) which concern identification of the coal, TG parameters which relate to the release of volatiles, or how fast the char burns and specific diagnostic temperatures at which identifiable processes start or end. By comparing data from different coals and assessment of the numeric parameters, reconstructions of how different coals will burn can be made.

The final data abstracts for a range of commercial coal products from various collieries are presented in Tables 5.1, 5.2, and 5.3. This information, along with that presented in Tables 3.2, 4.2, 4.3 and 4.5, also show the degree of correspondence which exists between normal analysis and TG derived parameters. Determination of the classification symbols of the coals (Table 5.1), is the first step in the analytic procedure. The classifications based on standard and TG derived proximate analyses, are shown in conjunction with the microscopic determinations. Parameters usable for classification and specification which were computed, using the formulae furnished by Snyman et al (1983), are shown in Table 5.2. Specification temperatures are shown in Table 5.3.
In order to use the two component concept of combustion results from TG dispersion analysis, the analytic test S(1,1,2) need to be considered because this data provides a good idea of how the

TABLE 5.1*

CLASSIFICATION RESULTS BASED ON COMPUTED HYDROGEN AND CARBON AND PROGRAMMED SEYLER PLOT

S. #	Microscopic & 1986 Assay	Proximate analysis		
		1984	TG	1986
1	V/D/0	VI/D/0	VI/D/2	V/D/0
2	III/D/3	II/D/4	III/E/4	III/E/4
3	V/D/0	VI/E/1	V/D/3	V/D/0
4	III/C/0	III/D/1	III/D/3	III/D/2
5	II/D/0	III/D/4	II/D/2	II/D/2
6	II/B/1	II/D/4	II/D/3	II/D/4
7	II/D/0	II/D/3	II/D/3	II/D/4
8	III/D/1	II/D/4	III/D/3	III/D/4
9	III/C/0	II/D/4	III/D/3	III/D/3
10	V/C/0	V/D/0	V/D/3	V/D/1
11	II/C/0	III/D/5	II/E/4	II/D/4
12	III/C/0	IV/E/5	III/D/4	III/D/4
13	II/A/0	II/D/2	II/D/2	II/D/2
14	II/D/1	II/D/4	II/D/3	II/D/5
16	II/C/2	II/C/7	II/C/7	II/D/2
15	II/C/9	II/B/8	II/D/9	II/B/9
17	III/D/5	II/A/8	III/D/4	III/B/8
18	II/C/8	II/A/9	II/B/9	II/D/9
19	II/D/8	I/A/9	II/C/9	II/A/9
20	II/C/9	II/B/9	II/D/9	II/B/9
21	II/C/9	II/A/9	II/C/9	II/A/9
22	II/C/9	II/B/9	II/D/9	II/B/9

* Reduction formulae furnished by Snyman (1983 p15 & 18)

TABLE 5.2

GENERAL DERIVED CLASSIFICATION AND SPECIFICATION PARAMETERS

S. #	@	COMPUTED VALUES				
		Dry ash (%)	Vitrinite (%)	Rov max (%)	HGI (%)	dC (%)
1	84	32,5	28	0,53	65	11,1
	TG	31,0	30	0,86	53	17,2
	86	28,6	26	0,60	60	10,8
2	84	14,5	21	1,01	52	11,1
	TG	17,6	18	1,02	52	8,7
	86	17,6	19	1,01	52	10,1
3	84	33,0	20	0,75	53	12,3
	TG	25,5	24	0,94	52	13,4
	86	25,8	24	0,66	56	11,9
4	84	18,7	23	0,78	53	14,6
	TG	18,2	24	0,93	52	13,6
	86	19,2	28	0,80	52	15,0
5	84	17,1	27	0,95	53	16,9
	TG	13,3	31	0,85	52	18,4
	86	13,7	31	0,99	55	17,9
6	84	12,4	33	0,95	55	22,0
	TG	12,0	25	0,90	52	14,3
	86	12,1	32	0,98	55	18,2
7	84	11,8	28	0,94	53	17,8
	TG	12,3	26	0,91	52	14,6
	86	12,8	28	0,96	53	15,7
8	84	14,6	25	0,96	52	13,9
	TG	15,6	25	0,93	52	14,4
	86	15,6	24	0,98	53	12,6
9	84	12,4	32	0,96	54	19,3
	TG	17,7	24	0,94	52	13,4
	86	17,3	31	0,91	53	17,6
10	84	25,3	27	0,72	55	18,5
	TG	26,9	24	0,94	52	13,3
	86	25,1	24	0,75	54	15,9
11	84	16,5	27	1,03	55	16,1
	TG	13,7	19	1,01	52	10,1
	86	14,4	29	1,02	55	16,3
12	84	20,4	20	1,08	56	13,7
	TG	19,2	22	0,97	52	11,7
	86	19,6	31	0,98	55	17,1
13	84	10,6	36	0,86	53	23,0
	TG	10,5	36	0,81	53	22,4
	86	10,2	37	0,86	53	22,2

* Explanation of symbols on next page

TABLE 5.2 (continued)

S. #	@	COMPUTED VALUES				
		Dry ash (%)	Vitrinite (%)	Rov max (%)	HGI (%)	dC (%)
14	84	14,1	29	1,00	54	18,5
	TG	10,4	26	0,91	52	15,2
	86	10,6	30	1,05	57	17,1
16	84	13,6	50	1,21	66	18,7
	TG	11,4	31	0,85	53	18,8
	86	11,5	54	1,21	67	20,0
15	84	12,3	65	2,40	49	0,5
	TG	12,2	39	2,41	41	1,4
	86	13,8	79	2,27	56	2,7
17	84	12,4	90	1,45	77	13,2
	TG	17,6	23	0,96	52	12,4
	86	17,7	75	1,42	73	11,2
18	84	8,9	50	1,60	40	2,3
	TG	10,4	40	2,40	40	-1,7
	86	11,5	99	2,30	61	1,3
19	84	8,7	100	2,40	59	2,4
	TG	13,1	45	2,30	44	-0,4
	86	13,0	100	2,40	60	2,4
20	84	13,2	68	2,30	51	0,9
	TG	12,0	35	2,40	38	-2,1
	86	12,5	67	2,71	43	-2,6
21	84	14,2	82	2,50	49	2,5
	TG	14,5	43	2,30	42	-0,9
	86	14,5	86	2,60	50	-0,4
22	84	10,5	65	3,10	35	-3,2
	TG	12,3	37	2,50	38	-2,3
	86	11,8	70	3,03	37	-2,7

S. # = Sample reference number
@ = Origin of data: 1984 Assay, Thermogravimetry, 1986 Assay
GTR = Grade/Type/Rank
HGI = Handgrove grindability index
dC = Carbon in volatile matter

TABLE 5.3*

TG DETERMINED SPECIFICATION TEMPERATURES AND OTHER RELEVANT DATA

S. #	TG °C	TW °C	TX °C	TS °C	TO °C	TIC °C	TCO °C	D2TGi mg/min²	ox mg
1	61	140	227	297	324	392	566	10,4	1,9
2	39	118	227	319	370	424	626	8,5	5,3
3	43	135	231	293	340	385	558	15,8	1,0
4	48	131	231	320	341	389	627	8,0	3,3
5	35	122	236	302	324	389	648	7,8	3,8
6	56	113	223	293	324	424	648	5,6	3,2
7	39	113	227	310	352	424	734	11,3	3,2
8	39	113	231	332	354	402	679	4,7	3,5
9	43	118	227	315	324	424	644	6,3	3,9
10	35	118	240	302	324	393	631	8,8	2,0
11	30	118	236	310	357	407	631	7,7	3,7
12	30	112	231	315	357	424	635	6,4	6,0
13	35	144	214	306	324	415	622	5,2	2,5
14	39	126	210	293	324	415	689	6,9	6,2
16	39	96	236	323	357	442	723	6,2	5,2
15	61	135	262	376	437	472	815	7,2	4,2
17	43	140	249	345	392	446	721	6,4	4,7
18	35	126	258	372	422	459	813	5,9	5,1
19	35	118	271	367	436	468	804	6,7	4,7
20	48	144	249	420	490	505	756	10,0	3,7
21	47	130	245	375	466	492	808	9,7	6,6
22	40	128	243	422	512	523	817	12,6	3,1

* Explanation of symbols on next page

TABLE 5.3 (continued)

EXPLANATION OF SYMBOLS

S. # = Sample reference number.

TG = Temperature where gas release terminates.

TW = End temperature for release of intrinsic water.

TX = End temperature for stable mass heating.

TS = Temperature of start of dispersion.

TO = Temperature where stable dehydrated mass value is again reached after absorption of oxygen.

TIC = Temperature where the partly carbonised coal, (ie. only high volatiles are present) is ignited.

TCO = Temperature at end of burning third order stage where furnace temperature is same as that of the sample.

D2TGi = Peak value of the rate of change in the rate of mass loss expressed in a convenient unit.

ox = Quantity of oxygen, expressed in mg, absorbed by the particular sample (usually 300 mg).

volatiles are released and the char is burned. It does not represent conventional burning of coal but identification of the predominant processes is possible by this slow heating of the coal and more detail can be obtained about the volatile content.

Volatiles released when coal is heated can assume a variety of components depending on the composition of the coal and the manner in which it is heated. For classified coals it can be expected that the volatiles which are released would comprise similar chemical compositions for similar processes. The volatiles must originate from the macerals which predominate for a given coal classification and rank. In order to gauge this aspect for the entire range of test coals Figure 5.1 was prepared.

The group of samples is considered as a data set which is arranged in ascending order of rank. Coals of the same rank are arranged so that the vitrinite content increases from left to right. Other corresponding maceral composition values are plotted as columns each with an individual ordinate scale. The points are joined by straight lines to show up as a curve; only to facilitate comparison: each coal is an individual entity which is shown in a group relation with others.

The groups are divided by a vertical line for distinguishing between bituminous coals and anthracite. A further subdivision which enables identification of low, medium and high ranks, is also introduced by a second vertical line. In order to subdivide the groups into high, average and low percentage categories, average strips are identified by inspection as shown. Low and high groupings are identified by black and white colouring. This enables easy reference to group characteristics in terms of predominant maceral compositions eg sample No 3 contains low (VI), medium (EX), low (RSF), high (IN) and high (VM).

For establishment of a link between the release of volatiles and possible macerals as sources, the group characteristics of the set of commercial coal products require attention. Figure 5.1 shows that for part of the low rank coals vitrinite is the dominating component while exinite, although present in smaller

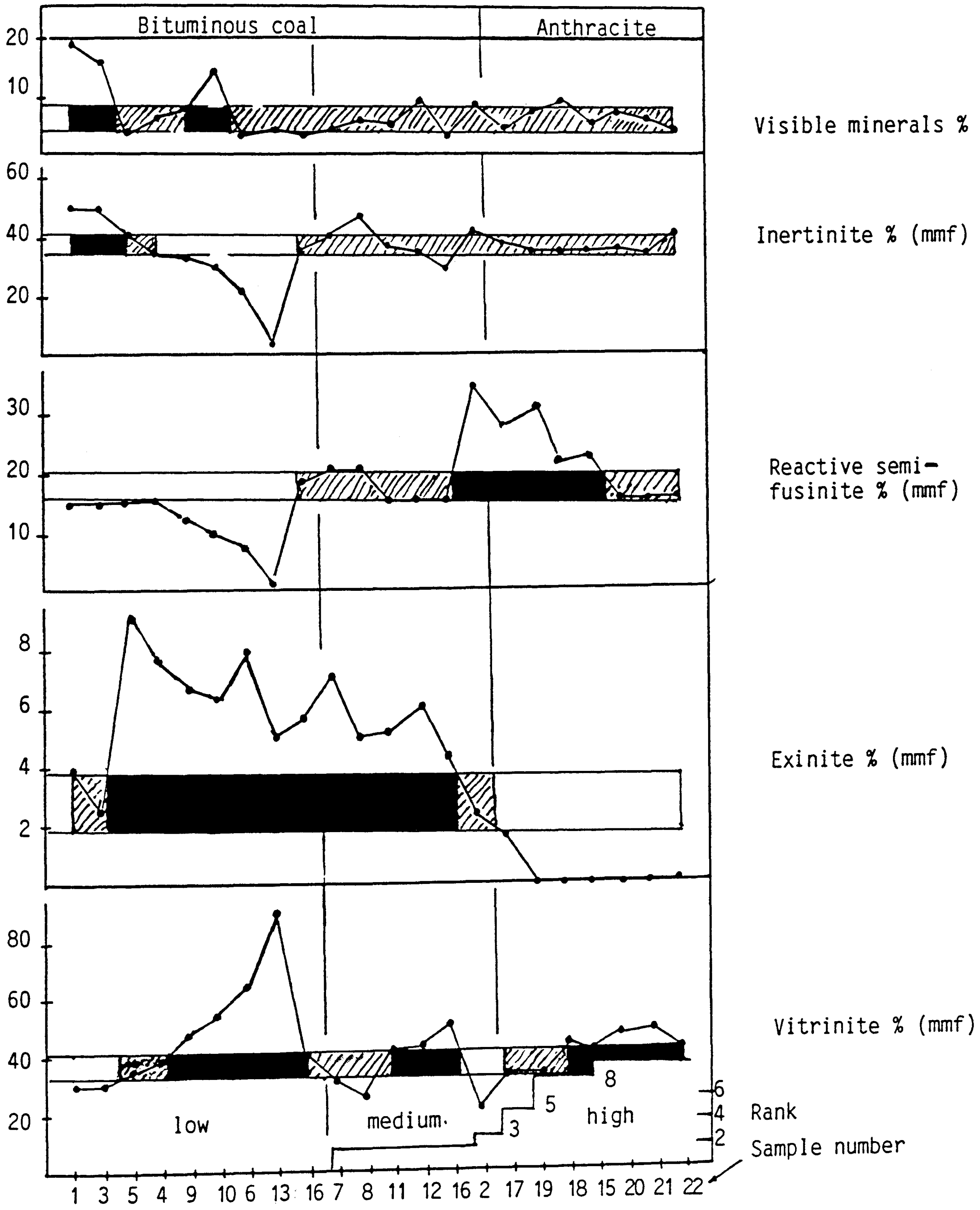


FIGURE 5.1 The maceral distribution of the group of test samples in relation to rank

amounts, predominates within virtually the complete bituminous coal sector ie incorporating low and medium ranks. It is absent in anthracites. Reactive semifusinite predominates in the anthracites for which the vitrinite content is average. Inertinite and visible minerals are only high for two samples viz. No 1 and 3 for which all other macerals are low. It is evident that the amounts of vitrinite and exinite, and reactive semifusinite to a lesser extent, are the macerals which will dominate the response of a given sample.

Figure 5.2 bears out the relations between the TG derived diagnostics and the predominant macerals contained in the group of samples. For classified coals the dispersion history S(1,1,2), should reveal by means of the specification parameters how the coal should behave under burning conditions. Through the model of Solomon (1981) the stages and phases in the dispersion cycle could be explained and it is now attempted to link the volatile products and the residue (pseudochar) burn out with the components of the coal which are most likely to dominate the course of a burning event.

The sequence in which the TG data in Figure 5.2 is shown in relation to the macerals has no significance: any curve can be compared with any maceral pattern over the range of samples. TG data are plotted in a similar manner to Figure 5.1 in conjunction with the codings which represent maceral dominance in the samples. On the basis of the predominance concept Essenhigh (1970) it is expected that anomalies in the parameter data which correlate with either black or white codings are associated with the predominance or lack of the maceral in the samples. Continuity across the the data set merely confirms the validity of a given correlation.

The curve for the light volatile component (lv), which is released before ignition occurs in a S(1,1,2) test, shows a general pattern of easy release for bituminous coals of rank < 5. For high vitrinite bituminous coals however light volatiles are liberated abundantly. Anthracites have a very low output of volatile matter before the pseudochar ignites. It can therefore

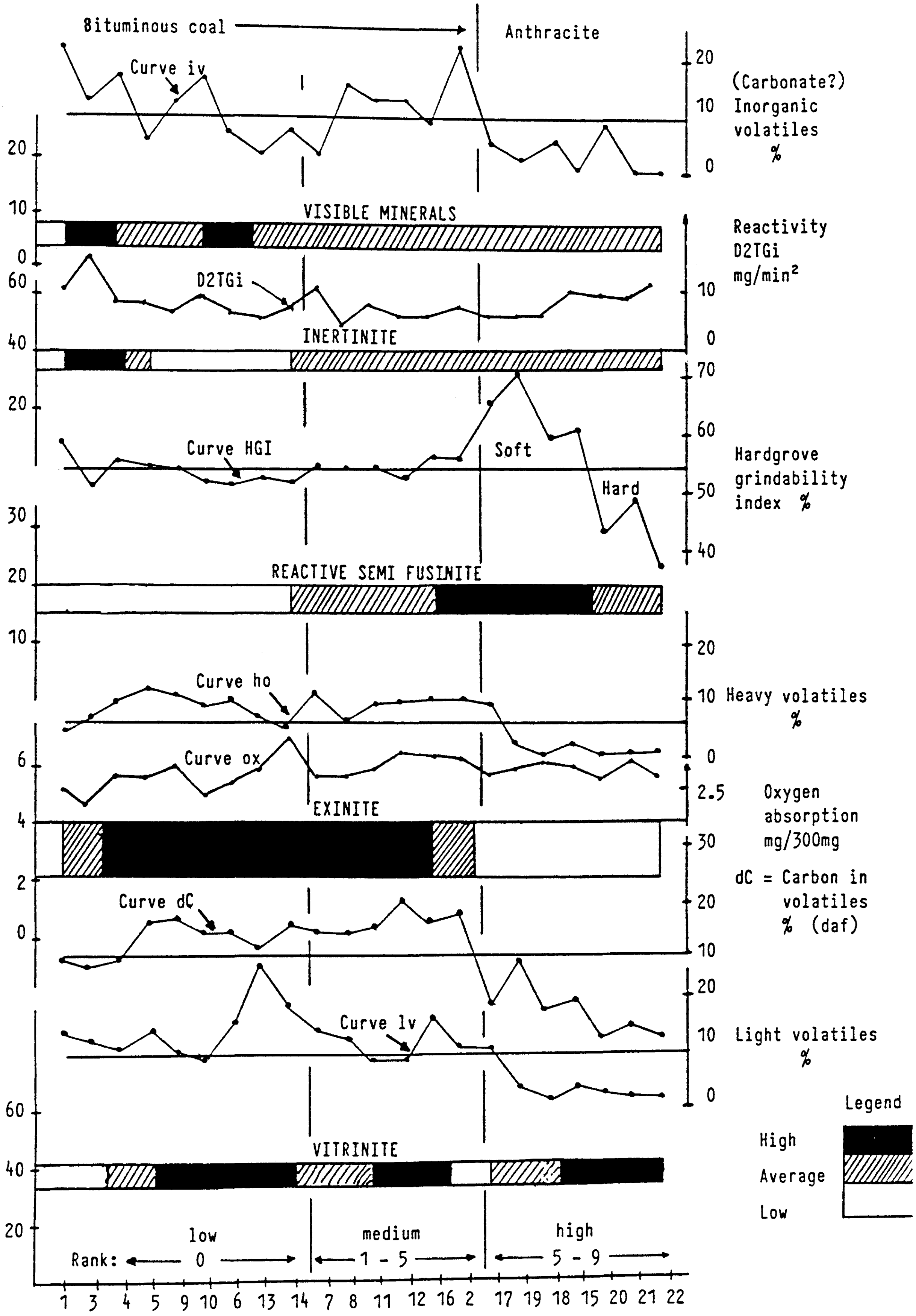


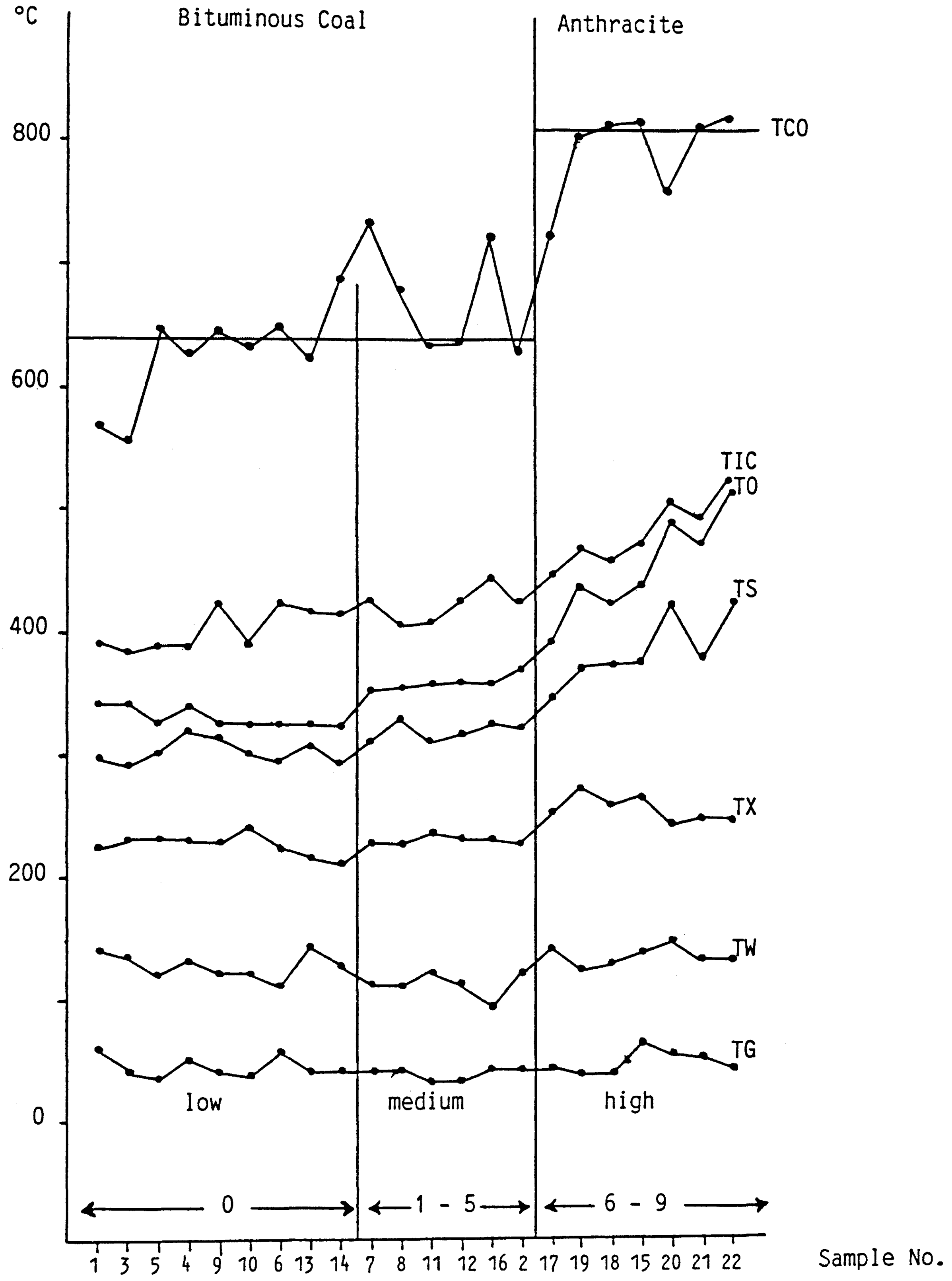
FIGURE 5.2 Correlation of TG parameters with maceral composition of the group of test coals

be expected for coals which liberate lv values in excess of say 12%, that those coals should contain relatively high vitrinite contents. In accordance with the model of Solomon (1981) and the analysis of Juntgen <u>et al</u>, (1979) it is expected that the light volatiles will consist of low order aliphatic compounds such as methane or ethane. This should ensure an inflammability aureole for these coals but conflagration of the pseudochar need not necessarily be guaranteed. The ability to determine the specific volatile component lv, of the total amount vm , which can be liberated, as well as the temperatures required for its exclusive expulsion TS and TIC (Figure 5.3) show how TG analysis can assist to assess a burning attribute of coal.

The (DAF) percentage of carbon contained in the volatiles dC, which is associated with the volatiles for the normal paraffin series relates to the calorific value ie the quality of the volatiles. The calorific value of methane is 37.7 MJ/kg and for butane it is 121,8 MJ/kg. The dC curve in Figure 5.2 shows that, excepting samples 1 and 3, a reasonably constant quality is maintained for all bituminous coal products. For anthracites the dC value (total carbon - fixed carbon) is very low, suggesting that relatively poor quality light volatiles are released. Inflammability of anthracites should be lower than for bituminous coals.

Exinite, although present in relatively smaller proportions than any other maceral group, is well represented over the range of bituminous coal samples. It was however shown, Figure 4.15, that exinite releases the major fraction of its volatiles at a temperature (435°C) which is higher than the average TIC value for bituminous coals. It liberates 15% as a lv fraction and 25% as (ho) ie the heavy volatile fraction (vm - lv). The role of exinite both as a stimulant for inflammability and guarantee for supporting deflagration appears very important.

The correspondence between the dC and ho curves (Figure 5.2) confirms this surmise (The volatiles vm of the commercial coals are reasonably free from harmful components ie ho in this case represents mostly combustible organic volatiles). The dips in the



<u>FIGURE 5.3</u> Specification temperatures derived from dispersion analysis

ho curve for samples Nos 14 and 8 however suggest that incombustible effluents which derive from the inorganic materials me, are present.

Although dC, unlike lv, is not exclusively derivable from TG data it can also be obtained from quasi-proximate parameters which constitutes its link with TG analysis.
The aptitude for inducing the formation of oxycoal, ie enhancement of chemisorption of oxygen prior to burning of the coal, is expressed by the ox curve for the sample set. It has not been ascertained whether charging of coal with oxygen, through heating it to the correct temperature, TX to TS (Figure 5.3), enhances burning or not. The ox curve shows that on the average bituminous coals adsorb about 2,5 mg of oxygen per 300 mg sample while anthracites adsorb about 5 mg. The mean excitation temperature is around 250°C which is a readily acquirable level for treatment of coal prior to burning it.

As a gauge of hardness (grindability) the HGI curve shows that all the bituminous test samples are comparable but that the anthracites show both low and high values. These parameters have no particular relation with TG observations, it is only shown because it can also be computed from the quasi-proximate values. Although not related to burning properties of coal it conveys information which has practical value relating to the relative fineness of the coal powder.

Relative "reactivities" ie D2TGi values, are also presented in Figure 5.2. The overall propensities for burning ie aptitudes for the pseudochar to conflagrate are virtually constant over the range of bituminous coals assuming values between 5 and 7 mg/min. Even some of the anthracites maintain this level of activity but the rest show values which are nearer to 10. Tests on inertinite show a comparable value of 7,8, vitrinite 15,8 and exinite 186 mg/min^2. This shows that the series of test coals all show values which are below the vitrinite level and even lower than inertinite: it is likely that the maceral type is only partly responsible for producing a characteristic D2TGi value. If this was not so it would be difficult to explain values which are lower than that for inertinite.

While considering the abovementioned attention should be given to the first two samples which show D2TGi values which are in excess of 10 mg/min^2 but low to average values for all macerals except inertinite and visible minerals. The carbonate inorganic volatiles are high for both samples. The crux of this situation is to explain how such high reactivities are possible for these coals which are poor in the more reactive maceral groups. It should be borne in mind that the iv curve expresses, most probably, carbonate effluents which are generated after the volatile release during conflagration of the pseudochar has already occurred. The likely explanation seems to be that pyrite releases volatiles during an oxidation process in two stages. At first, ie during deflagration of the pseudochar, the pyrite is partly oxidized vigorously to leave a lower order sulphide which is only oxidized at much higher temperature ie when the carbonates are normally decomposed.

The fact that reactivity can be affected by other reactants than the standard components which are assumed to dominate the burning process stresses the "multicomponent heterogeneous" nature of coal and the remark of Dobal et al, (1982): "Interpretations must be made with caution".

The specification temperatures are presented in Figure 5.3. These sets of temperatures which designate limiting conditions for reaction stages within the lower ranges resort to almost constant values which apply to either bituminous coals or anthracites. The three temperatures TS, T0 and TIC show features which are broadly similar for all three instances. A definite regression tendency is expressed between rank and these temperatures. For the temperature value T0 (Figure 3.12) a regression relation was established which enables the determination of the rank (R), of a coal using this TG parameter. The expression is:

$$R = 0,00009469(T0)^2 + 0,1326(T0) - 32,4$$

Values for TCO vary more randomly which is to be expected because it depends on the vigour with which burning occurs for a specific coal inclusive of all the complex reactions to which it could be subjected.

In contrast to the inferences regarding burning which are deduced from dispersion data more directly determined parameters are obtained from tests S(3,1,2) which involve actual burning of coal samples. For this case also a two component analysis is involved namely the liberation of volatile matter and subsequent burn out of the char.

Based on experimental results a mathematical relation, of the form At - Dt^2 , can be established between burn out times of volatiles and char for specified ambient thermal conditions. These empirical equations are governed by coefficients which are diagnostic for the particular coal. A parameter which expresses the drive associated with the burn out process is referred to as the A or activation parameter which has dimensions mg/s. In contrast to this stimulus for reaction, there exists another parameter which expresses a damping effect which is superimposed on the burning drive, which tends to retard the reaction process. This is referred to as the D parameter with dimensions mg/s^2.

The A and D coefficients are not independent of each other, they only depend on the amount of char to be burned and the time taken for burning to be completed.

The volatile expulsion can be analysed on a similar empirical basis but since the time for volatile release is of the order of ten times less than that of the char it is of more practical importance to consider the total amount of volatiles which are released immediately after exposure of the sample to the high ambient temperature of about 1000°C. A further aspect which is important is the manner in which the volatile release function merges with the burn out curve of the char. If continuity is maintained (Figure 3.20) it shows that the char was ignited while volatiles were released but if a break shows up between the curves it means that the char was ignited after all volatiles were relesased.

The relation of the initial quantity of S(3,1,2) volatiles released, to vm, the total percentage possible, provides an indication of the retention potential of the char for volatiles. If more volatiles are retained to burn along with the char, smooth and persistent burn out is usually assured.

Continuity between volatile conflagration and ignition of the char is important because if the volatiles burn out before the char is ignited it smoulders and a time lapse is introduced which hampers the sustained generation of heat. The fuel thus fails under load, particularly for PF burning conditions.

To illustrate one specific application and analysis of drop furnace techniques, results from a study which was executed on coal with a specific combustion problem, will be discussed. Note none of the commercial coal products reveal specific burning problems: they are all coals which are used in industry.

The problem was encountered during the pilot plant testing of a coal to be used in a PF furnace. While being tested the coal burned well with appropriate excess air but when a heavy coal load condition was introduced the coal suddenly failed to ignite and liquid fuel was required to support combustion.

A TG test program was planned in which the -70 mesh coal sample which was provided could be used. The coal was subjected to a dispersion analysis which provided the following information:

1. The quasi-proximate values obtained were;

as	vm			dC
	22,7%			12%
	lv	ho	iv	
22,0%	14,6%	**6,6%**	1,5%	

2. Some of the specification parameters are;

TS	TO	TIC	(°C)
340	380	**464**	

3. The classification symbol was determined as V/E/0

For purposes of comparison a similar coal which is known to perform satisfactory under PF conditions, for which data were available, was selected. The characteristics are as follows:

1.

as	vm	dC
26,3%	25,4%	15,9%

lv	ho	iv
8,%	15,5%	1,8%

TS	T0	TIC	(°C)
284	336	371	

2. The classification of this coal is V/C/0.

Important differences which are notable are:

a. The high amount of light volatiles 14,6%, which was released by the test sample in contrast to the 8,0% in the case of the reference sample.

b. The small amount of volatiles which was retained 6,6% vs 15,5%, by the test sample for burning with the char.

c. The high temperature at which ignition occurs 464°C vs 371°C for the reference sample. The lower value for dC (12%) and the type E symbol vs 15,9% and C points to a low vitrinite content for the test sample which in view of the high TIC could point to possibilities for ignition problems. A provisional surmise could be that the test sample under severe thermal stress could fail to ignite and sustain burning.

The normal drop furnace tests for the reference and test samples showed that the former has an activation coefficient A of 1,68 mg/s vs. 1,558 mg/s and the respective damping coefficient D is 0.0056 mg/s^2 vs 0,00382 mg/s^2. These values show very similar volatile burn out curves but it is notable that the test sample, when exposed to a high thermal gradient, initially disposes of all its volatiles (22,7%) while the reference sample burns away only 22% of its total amount of 25,4%. Further investigation of the volatile release in relation to burning is thus evident.

The test sample was split into three grain size fractions viz -0,2 to +0,105 mm, -0,105 to +0,075 mm and -0,075 mm. To ensure good oxidation conditions 200 mg samples of each of these grain fractions of the original sample were subjected to S(3,1,2) applications. The A values for all three samples were with minute variations 1,43 mg/s and the D values likewise 0,0053 mg/s². This shows that the char burnouts were virtually identical but the significant differences could be noted from the burn out curves. The burn out curves for the volatiles of the average 0,152 mm and 0,087 mm grain sizes showed discontinuity between the volatile and char segments of the burn out curves. The volatile curves were terminated by "no mass loss" stretches of 3,5 and 3 seconds respectively before the mass loss of the char fraction commenced. For the -0,075 mm fraction a continuous curve was observed.

This showed that the larger grains which normally constitute a fraction of the test sample were prevented from ignition probably as a result of the lack of retained volatiles which could assist burning in a depleted oxygen environment. To resolve this problem, finer grinding and/or better oxygenation and/or blending may be applied. The small grain fraction, apart from the reduced particle size, probably also has a different composition which could sustain ignition and support subsequent burning.

Increased air feed was tested for similar grain groupings and for all cases continuous burn out curves were obtained.

There are various problems associated with coal which can be resolved by application of the entire range of thermal analytic procedures S(i,j,k) with discretion and also routine aspects such as the determination of the range of parameters but the most important aspect to realize is that the observed data must be interpreted in order to obtain real use from them: this aspect cannot be put into a routinised form. An attempt was made to provide guidelines which were substantiated by various experimental applications as well as a scrutiny of the information furnished by other observers.

6 CONCLUSIONS

Thermal analysis comprises an integrated system for assisting with the determination of the burning properties of coal. The system, of which DTA and TGA are important members can be expressed in a more generalised form by considering the temperature application, reactant types and reaction environments as indexes of a matrix S(i,j,k). Through the use of computerised control and reduction any of the experimental states expressed by the matrix can be applied using a single hardware unit which is operated using different software.

Due to the complexity of coal as a chemical substance its reactions, particularly under oxidizing conditions, are heterogeneous and stochastic with the result that a single fundamental interpretation for the results is not always possible. Determination of standard reaction parameters such as a rate constant or activation energy is not possible because these are properties which pertain to a specific molecular reaction. Since TG techniques always record the result of groups of unknown reactions it is not usable for quantitative stoichiometric computations when coal is analysed.

A systematic manner can however be developed by which unambiguous analysis of TG data can be made on an empirical basis. Application of this analysis leads to obtaining of additional informative data from eg proximate analysis parameters.

In order to optimise the interpretation of the TG specification parameters it is essential that the coal be categorised so that only properties of corresponding kinds of coals can be compared to each other. This is done on the basis which was established by petrographic analysis and uses as diagnostic indicators the grade, type and rank of the coal.

Burn out of coal, broadly speaking, consists of two major components viz. volatile combustion and char burn out. Both processes follow empirically determinable mathematic functions: char in general follows a zero order mechanism.

The prime features of volatile release and burning are dominated by the maceral composition of the coal. Vitrinite and exinite act as the major controls of propensity for burning. The predominant effects of maceral control over burning can be identified through TG analysis. This study was only touched on and more research is required.

Ash content of coal did not show up in the present study as a major controller of burning. If the correct maceral content is present the coal seems to burn with little regard for the ash content. Ash, up to a limiting value, seems to present more of a nuisance value, that is , its presence reduces the amount of burnables in the coal and consequently the burn out time per charge is reduced. Furthermore, handling of large quantities of ash presents a technological challenge to the design of furnaces to deal with a large throughput of coal.

There are several avenues yet to be studied in detail. These include the process and significance of the formation of oxycoal, the implication and significance of the gas and water released in the first main stage and the surmised sublimation of metals which occurs in main stage 5.

Techniques which require further study are DTA for identifying the smaller exothermic reaction in greater detail and the piecewise burn out technique S(2,1,?) for following up the process of specific phase reactions within the dispersion process.

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