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Proton magnetic resonance thermal analysis in coal research: A users overview[1]

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Abstract

An overview of the principles, capabilities, and applications of proton magnetic resonance thermal analysis (PMRTA) is given. Its range of possible applications is described and results from some recent studies are discussed. PMRTA enables the dynamic state of materials with significant hydrogen contents to be investigated during pyrolysis.

This is a thermal analysis technique which uses pulsed proton NMR 'broad line' spectroscopy as the means of determining the behaviour of the sample under investigation. Samples are subjected to a controlled temperature programme either ramped at a fixed rate (up to 20°C min^{-1}) from 40°C up to 600°C, or held at a fixed temperature within this range. ^1H NMR measurements are made at intervals throughout the temperature programme. These in-situ measurements allow the progress of thermal transformations to be determined. The solid echo signals obtained for a rigid lattice are representative of the entire hydrogen population of the sample and the peak echo is a measure of the total hydrogen content. Deviations from this situation during pyrolysis require corrections to be made. The hydrogen content can therefore be monitored semi-quantitatively in the residual sample throughout the temperature programme. Molecular properties affect the transverse relaxation signal so that the proportion and extent of hydrogen mobility can be determined. Thermoplastic events, material loss and interactions between materials can be detected and properties predicted using validated correlations with data from established methods of analysis. It may be applied to materials which contain a significant amount of H_2 and minimal moisture or magnetic material.

The instrument was originally developed at CSIRO, Australia, for use in the investigation of coals and related materials. Correlations of PMRTA parameters with a range of coal properties were established with a suite of Australian coals. At CRE the correlations of PMRTA parameters with coal properties have been developed further with a suite of UK and international coals. Recent studies have included investigation of a range of coal behaviours including the non-additive swelling of some coal blends (an important property for coals fired on grate stokers), coal spitting (of importance for coals burned in top feed stokers and domestic coals), effects of microwaving on coal properties (a technique being investigated with a view to reducing coal sulphur contents), coal spontaneous heating (a coal behaviour which it is not currently possible to predict because of the large number of factors involved), coking properties (coal plasticity and fluidity are crucial properties for successful coke production and PMRTA is a useful tool for investigating these properties) and behaviours of coal maceral concentrates. These are described and potential future applications for the technique, suggested. © 1997 Elsevier Science B.V.

Keywords: Analysis; Coal; ^1H NMR; Pyrolysis; Thermal

1. Introduction

NMR measurements are usually made under static temperature conditions. A range from −100° to +200°C is commonly available. In the early 1960s, measurements were made of coals and related materials at elevated temperatures, investigating the effect of temperature on the mobility of the hydrogen contained in the coal matrix [1,2]. In the late 1970s, the nature of polymer melts, pitches, and coal plasticity were investigated at temperatures in excess of 400°C [3–5]. More

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polymer melts, pitches, and coal plasticity were investigated at temperatures in excess of 400°C [3–5]. More recently, since about the mid 1980s, workers at the Commonwealth Scientific and Research Organization (CSIRO), Australia, have been developing a technique known as Proton Magnetic Resonance Thermal Analysis (PMRTA) [6]. This is a thermal analysis technique which utilizes dynamic proton NMR 'broad line' spectroscopy to measure changes which take place in the sample. It enables effects of temperature on hydrogen containing solids to be investigated. The sample is heated, usually under an inert stream of nitrogen from 40° to 600°C and the behaviour of the hydrogen, monitored.

This technique was developed for investigation of coals and coal-related materials. The temperature range is selected such that important changes occur in the coal structure including fusion, resolidification and the loss of a significant proportion of the 'volatile matter'. These properties have a significant effect on the way in which a particular coal behaves in a given utilization system. PMRTA enables measurement of these properties. Additionally, coal properties can be estimated by application of correlations between ^{1}H NMR parameters, measured by the system, and coal properties measured by conventional analytical techniques.

2. Technique description

The instrument is based on a Bruker Minispec pc120 system which is a high power pulsed NMR spectrometer operating at 20 MHz. This has been

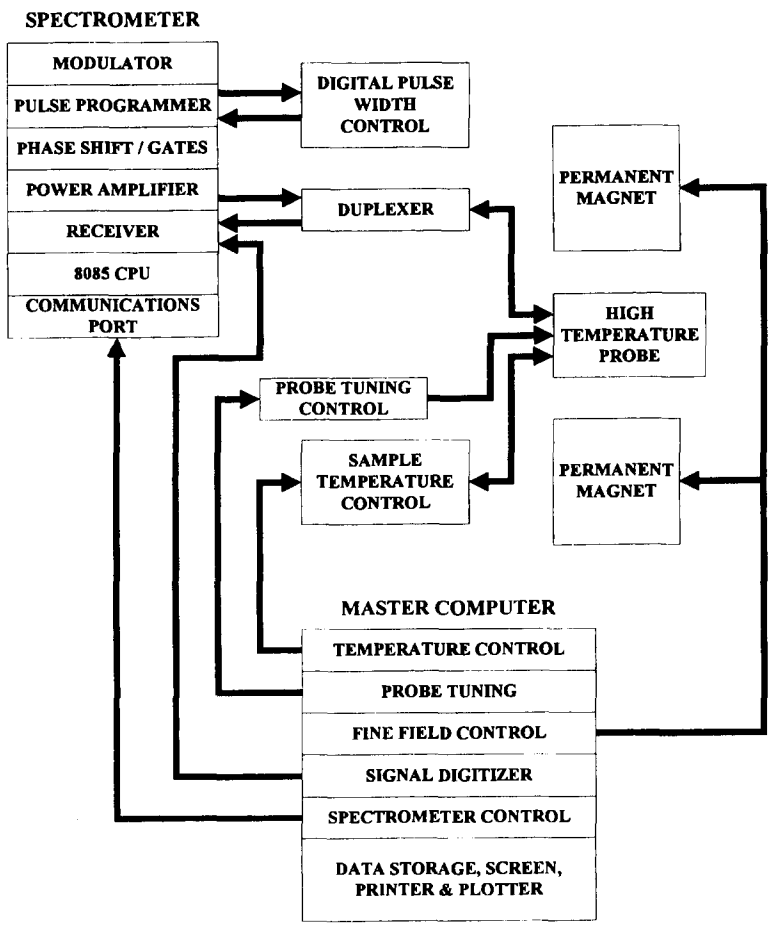

Fig. 1. The main components of the PMRTA.

modified to incorporate an electrically heated high temperature NMR probe [7], capable of operating at up to ~700°C with controlled heating rates of up to 20°C min^{-1}. The usual ramp rate when testing coals is 4°C min^{-1}. Temperature control is achieved using a control loop connected to a thermocouple mounted below the sample such that it does not interfere with the magnetic field. This thermocouple is regularly calibrated against a thermocouple mounted in a dummy sample. The PMRTA system configuration has been described in Ref. [7] and shown schematically in Fig. 1.

Samples are presented to the instrument in 8 mm outside diameter, flat-bottomed NMR tubes. A glass and PTFE assembly (Fig. 2) is fitted to the tube prior to insertion in the NMR probe. This enables an inert stream of nitrogen to flow over the sample and allow pyrolysis products to be drawn out of the sample tube. Samples range in size from 100–600 mg, depending on their hydrogen content. A rough guide for coals is to use a sample depth of 16 mm. Particle sizes of samples are limited by two factors: firstly, the need to fit into the tube, and secondly, the need for the sample to be sufficiently densely packed for the required sample size to fit into the measurement zone (25 mm). Some samples swell significantly and this imposes a limit on the amount of sample that can be used. Coal samples are usually ground to <500 μm or finer, shortly before testing. The presence in the sample of ferromagnetic species, either initially or by formation during pyrolysis, e.g. from siderite in solid fossil fuel, gives rise to anomalous behaviour [8]. Where this is a problem, samples may be acid washed with 1 M HCl to remove any soluble iron species, then rinsed with distilled water and dried under nitrogen at 105°C. Samples usually need to be dried to ensure that they contain no free moisture because water gives a very strong signal with a long relaxation time and leads to false indications of mobility and hydrogen loss from samples. Duplicate runs are usually carried out for each sample and the results, averaged.

The technique uses pulsed proton NMR 'broad line' spectroscopy. ^1H NMR transverse relaxation signals are generated by using a $90^\circ_x - \tau - 90^\circ_y$ pulse sequence to stimulate their nominal solid echo representation. Signals are captured over a 30 s period and averaged. The number of signals that can be collected in this period is dictated by the transverse relaxation

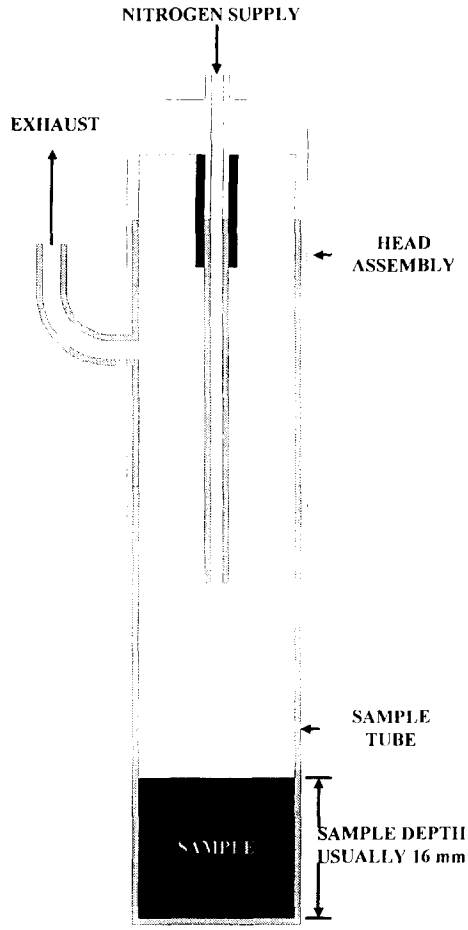

Fig. 2. The PMRTA sample tube assembly.

time for the sample at the current temperature. ^1H NMR signals are sensitive to temperature, hence a calibration of signal amplitude over the temperature range of the experiment is used. These calibrations are prepared using a sample whose hydrogen content is not modified during the heating cycle, i.e. a char sample, and are regularly updated.

The initial amplitude of the transverse relaxation signal enables the apparent residual H_2 content of the sample to be measured. Resolution of the transverse relaxation signal into Gaussian (rigid) and exponential (mobile) components (Fig. 3) allows the proportions of mobile and rigid hydrogen in the sample to be determined at each temperature.

The empirical second moment (M_{2T}) [9] calculated from the transverse relaxation signal is reduced from the rigid lattice value by molecular motion and this is

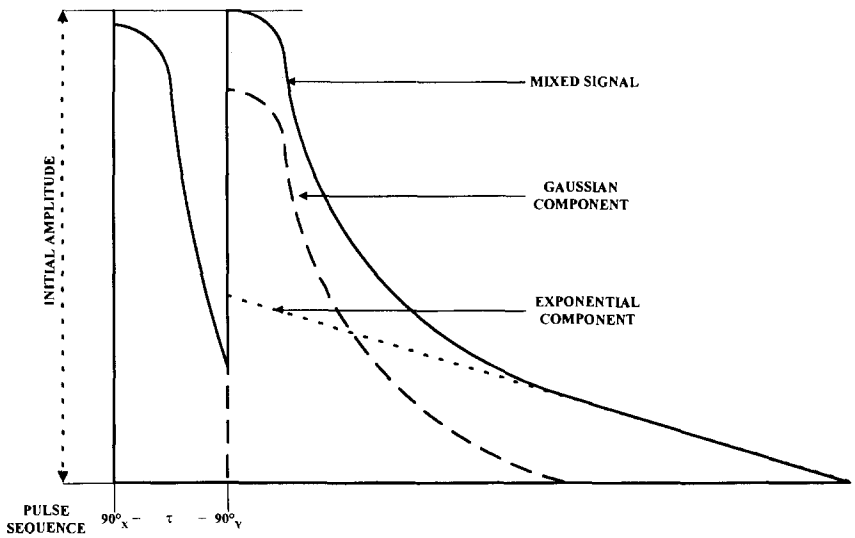

Fig. 3. Pulse sequence and typical transverse relaxation signal, showing its Gaussian and exponential components.

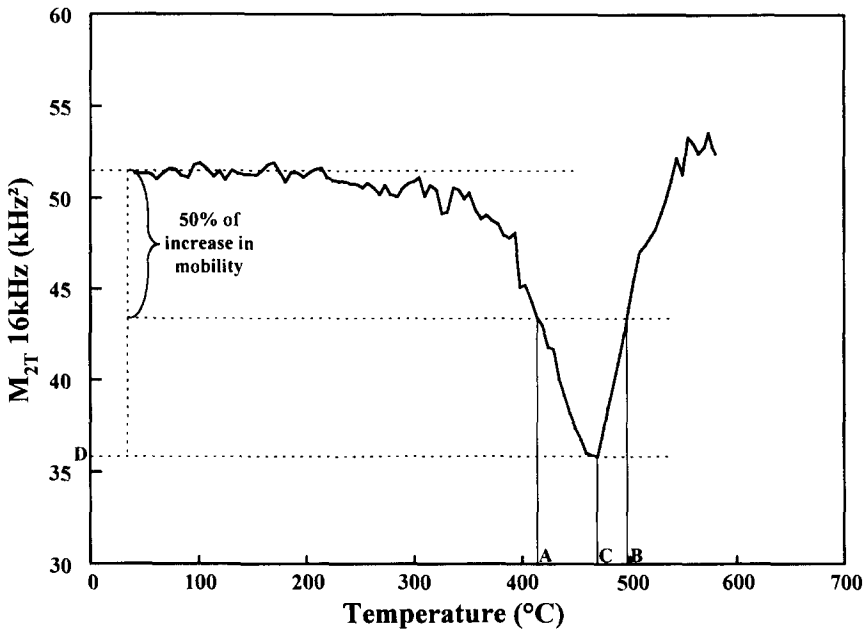

Fig. 4. A typical plot of $M_{2T}16$ against temperature for a bituminous coal. A – Temperature of onset of plasticity, B – Temperature of maximum fusion, C – Temperature of resolidification, D – Maximum plasticity.

used as a measure of the degree of mobility (52 – minimum, 0 – maximum) in the sample at each temperature. Values of M_{2T} over the temperature range are calculated using PMRTA data analysis software. They are calculated from part of the relaxation signal truncated at specific frequencies, 16 kHz ($M_{2T}16$), 25 kHz ($M_{2T}25$) and 40 kHz ($M_{2T}40$). Fig. 4 shows a typical plot of $M_{2T}16$ against temperature for a

bituminous coal and indicates how key parameters are determined, including temperatures of onset of plasticity, maximum fusion, maximum plasticity, and temperature of resolidification.

With the objective of providing a quick method for determining a range of commonly used coal properties, CSIRO developed correlations between values of M_{2T} at various temperatures and values for properties determined by conventional laboratory analyses. They have applied PMRTA to a range of studies of coals and related materials, including measurement of interactions between: different coals [10], coals and aromatic hydrocarbons [11], coals and infusible carbonaceous additives [12], coals and pitches [13], and evaluation of coking coals [14].

3. Summary of past, present and potential works at CRE

Several studies have been undertaken using PMRTA with the objectives of testing and extending its range of capabilities.

3.1. Prediction of coal properties

The first study tested the applicability of the correlations derived by CSIRO for prediction of coal properties and sought to enhance them by extending the range of coals used in their derivation [15]. The CSIRO correlations were based on measurements of a suite of 30 Australian bituminous coals (80–90% carbon, dry, mineral matter free basis). This study was carried out using an extended rank series of 51 UK and European coals (70–95% carbon, dry, mineral matter free basis). The CSIRO correlations were applied to the PMRTA data from these coals and, although it was found that they gave results of the correct order, the spread of the results was wider than would be acceptable for conventional analyses. In some cases there appeared to be systematic differences between the values obtained from the PMRTA and those from conventional analyses. Such systematic effects may be due to inter-laboratory differences or differences between the behaviour of coals from different geographic areas. The data collected for 45 samples of coals were used in the derivation of modified correlations. The remaining six formed a rank series of coals which were used to determine the validity of the new correlations. The range of properties studied and the quality of the initial predictions and the new predictions are given in Table 1. There was an improvement in the quality of the predictions for each of the coal properties but in most cases the correlations were not sufficiently accurate to replace the conventional test methods. However, it was concluded from this study that PMRTA could be used as a relatively quick method for screening the properties of a large number of coal samples.

Table 1
Quality of the original and modified predictions of various coal properties by PMRTA as indicated by the percentage of results falling outside the BS reproducibility or laboratory repeatability limits

Property	Limits	Percentage of results outside limits for original predictions	Percentage of results outside limits for new predictions
Carbon content, % daf	0.6 [a]	41	32
Hydrogen content, % daf	0.4 [a]	12	5
Moisture content, % ad	0.1	90	83
Volatile matter content, % daf	1.0	56	32
Calorific value, MJ/kg	0.3	40	25
Crucible swelling number	1	54	68
Gray King coke type	1	83	45
Hardgrove grindability index	3	73	46
Vitrinite reflectance, %	0.08	46	4
Vitrinite content, % mmf	6	72	61
Exinite content, % mmf	3	56	25

[a] The British Standard limits for these tests are 0.3 for carbon and 0.15 for hydrogen. However, the laboratory performing the chemical analyses was only able to acheive repeatability limits of 0.6 and 0.4 and so these are the limits that were used for the comparisons.

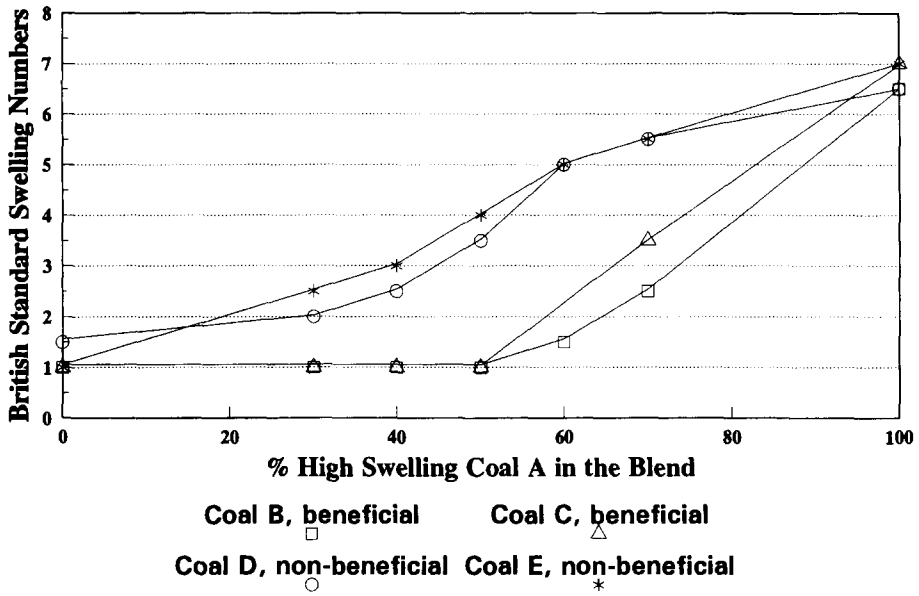

Fig. 5. Variation in British standard crucible swelling number with blend composition.

3.2. *Swelling properties of coal blends*

An important property for coals burned in stoker fired appliances is coal swelling. The swelling behaviour of coals on grates affects the permeability of the bed which controls the flow of air through it. If the swelling of a coal or coal blend is too high, it reduces the permeability of the bed which leads to poor combustion. When some coals are mixed they produce a blend with a crucible swelling number (CSN) [16] which is a weighted average of those for the blend components. In other cases, the behaviour of the blends deviates significantly from this pattern. These blends have swelling characteristics close to those of the low swelling component until the proportion of the higher swelling coal exceeds a level, usually ~50%. PMRTA provides a means of investigating the thermoplastic behaviour of materials and an investigation was carried out to determine why some low swelling coals produce this beneficial effect but others do not [17]. One high swelling coal was blended in various proportions with four low swelling coals. Two were known to have beneficial effects in reducing swelling properties and the other two did not. Blends of four coals were prepared containing 30%, 40%, 50%, 60%, and 70% of low swelling coals. The CSN for each of the individual coals and the blends was determined using the British Standard swelling test (BS 1016 Part 107). The variations of CSN with blend composition is shown in Fig. 5. PMRTA was carried out on each of the samples and the maximum mobilities and maximum amounts of mobile material showed significant differences between the individual coals (Table 2). These data alone did not identify the reasons for the effects of the beneficial and non-beneficial low swelling coals. Swelling is likely to be affected by both the thermoplastic properties and the physical structure of a coal. The porosity of each of the individual coals was determined by mercury porosimetry and the results are given in Table 2. Taking these results together with the PMRTA data, it appears that the low swelling coals with no beneficial effect on coal blends have a combination of the relatively high degrees of fusion and mobility of the high swelling coal but with much greater porosity, approaching those of the beneficial low swelling coals. This combination of properties not only prevents them from swelling, but also prevents any beneficial effect on blends.

3.3. *Coal spitting*

Coal spitting or coal particle explosion in top fed stoker fired boilers can lead to generation of excessive particulate emissions from the stack, tube erosion, and

Table 2
PMRTA, coal swelling, and porosity data for five coals used in the investigation of the non-additive swelling properties of coal blends

Coal	A	B	C	D	E
Swelling type	Low	Low	Low	Low	High
Crucible Swelling No.	1	1	1.5	1	7
Beneficial effect	Yes	Yes	No	No	—
Maximum extent of coal fusion	14.9	19.1	31.3	40.5	42.7
Maximum degree of mobility (52=rigid & 0=fully fused)	41.3	40.8	34.8	31.9	30.5
Porosity, $m^2 g^{-1}$	89.1	94.4	58.2	70.5	23.9

poor fuel efficiency. The method for testing coals for this property is to burn a sample in a domestic grate and observe the spitting behaviour. This is a qualitative test which requires a relatively large sample of large-sized coal. PMRTA was identified as a potential tool for investigating this behaviour. Samples of four coals known to give spitting problems were analysed and the results compared to those for normal, non-spitting coals. The $M_{2T}16$ values for the four coals were calculated and compared with those for a non-spitting coal. These data are presented as a pyrogramme in Fig. 6. This shows that the typical non-spitting coal remains rigid up to ≈300°C, where $M_{2T}16$ starts to decrease rapidly, indicating a rapid increase in molecular mobility. A similar pattern has been observed for ~50 non-spitting coals. In contrast, the $M_{2T}16$ values for the four known spitting coals decreased over a much wider temperature range, becoming significant above ~100°C. The more rapid decrease in $M_{2T}16$, if it occured, at all did not take place until ~350°C. The more rapid increases in mobility noted for both the non-spitting and spitting coals at >300°–350°C are caused by thermoplastic transitions and some decomposition of aromatic molecules. The gradual increases in mobility for the spitting coals starting at lower temperatures is believed to be caused by the softening of perhydrous aliphatic structures [18]. A simple way to quantify the differences between the samples is to use the value of $M_{2T}16$ at a specific temperature. In this case, 330°C was selected as appropriate and the values for the four spitting coals and the observed range for non-spitting coals are given in Table 3. These results demonstrate the potential for use of PMRTA identifying coals with this type of behaviour. However, further work would be required on quantifying spitting behaviour before

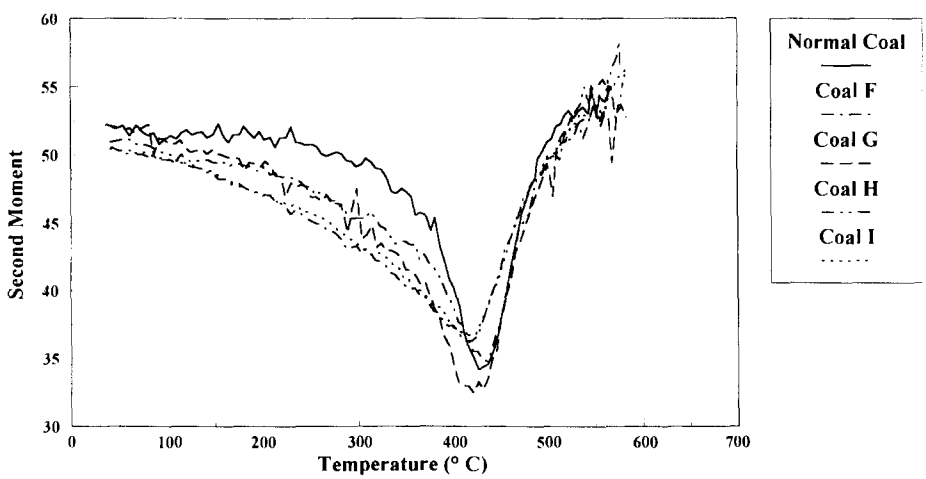

Fig. 6. PMRTA pyrogrammes showing the variation in $M_{2T}16$ over the temperature range for four spitting and one non-spitting coal.

Table 3
Coal mobilities at 330°C, as indicated by $M_{2T}16$, for four spitting coals and typical non-spitting coals

Coal	Spitting	$M_{2T}16$ at 330°C
F	Yes	41.7
G	Yes	43.3
H	Yes	44.4
I	Yes	42.2
Normal	No	47–49

quantitative predictions could be made from PMRTA data.

3.4. Properties of coking coals

There is a continuing need to improve the quality of coke produced for the steel industry while at the same time reducing costs by use of lower cost coals. This has led to a move away from the use of prime coking coals and attempts to use coals which previously would not have been accepted as coking coals. PMRTA, together with other elevated temperature NMR techniques, is currently being used to investigate the behaviour of coals during the important initial stages of the coking process where the major phase transitions and volatile matter loss occur, up to 600°C. The objective of this project is to identify better the methods of testing coals to determine their likely impact on coke quality. This work involves the study of a range of whole coals and maceral enriched fractions. Conventionally, the inertinite-rich fractions would be expected to be, as their name implies, largely inert. They are not expected to demonstrate any thermoplastic properties. Conventional test methods such as Geiseler plastometry support this view. However, when samples were analysed using PMRTA, small but significant degrees of molecular mobility were detected. This suggests that the inertinite macerals may have a more active role in the coking process than previously thought. Some coals available in the world market contain high levels of inertinite macerals, notably some Australian coals, and the conventional wisdom is that they would not be suitable for use as coking coals. However, they are used for this purpose in Australia and produce acceptable cokes. PMRTA of inertinite-rich fractions of some Australian coals have indicated that the inertinite macerals are much more reactive in terms of thermoplastic properties than those in northern hemisphere coals. These studies suggest that, with further development, PMRTA could be a valuable tool for selecting coals for inclusion in coking blends.

3.5. Spontaneous heating of coal

Spontaneous heating of coal in stockpiles or silos has a detrimental effect on coal quality due to the oxidation of coal. Under some sets of conditions, fires and even explosions can occur. Prediction of this type of behaviour is extremely difficult because of the range of factors involved and the difficulty in measuring them. Some of the key factors are: coal properties, ambient temperature, mass of stored coal, and ventilation. Previous studies have indicated that hydrogen release is indicative of the probable behaviour of a coal, with spontaneous heating being more likely for coals giving higher levels of hydrogen release [19]. This suggests that PMRTA could be a suitable tool for investigating this behaviour. A limited initial study was carried out. Samples of three UK bituminous coals and a sample of wood waste were tested. Wood was selected as a comparative sample to represent uncoalified biomass. The intermediate materials between this and bituminous coals are peats, lignites, and brown coals. It is generally the case that the lower the degree of coalification the greater the tendency to spontaneously heat and ignite. A significant difference would therefore be expected between the behaviours of the wood and coal samples. A temperature ramp from 40°–100°C at 1°C min^{-1} with a hold time of 2 h was selected as suitable on the basis of the likely conditions in a spontaneously heating stockpile and the conditions used for spontaneous combustion tests [20,21]. The samples were dried under vacuum at

Table 4
The percentage of hydrogen remaining in three coal samples and a wood sample after heating at 110°C and the temperature at which maximum hydrogen loss was recorded

Sample	%H remaining	Temperature of maximum H loss, °C
Coal K	47.4	101
Coal L	91.3	69
Coal M	93.0	79
Wood	75.3	63

≈45°C, rather than the usual method of drying under nitrogen at 105°C as this would have caused the changes to occur in the sample before they were run. The results for the four samples tested are given in Table 4. They indicate that the three coals lost small amounts of hydrogen – <10%, but that the wood sample lost ~25%. It is thought that the higher the hydrogen loss at low temperatures the greater the tendency of the material towards spontaneous heating. This result indicates that PMRTA may be a useful tool for predicting this type of behaviour. However, further investigations of the nature of the hydrogen loss from the samples, whether it as H_2, CH_4, etc., or as release of inherent H_2O, and of the behaviour of a much wider range of samples, are required with subsequent validation.

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