

*Review Paper*

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**THERMAL ANALYSIS APPLICATIONS  
IN FOSSIL FUEL SCIENCE**  
**Literature survey**

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**Abstract**

In this study, instances where thermal analysis techniques (differential scanning calorimetry, thermogravimetry, differential thermal analysis, etc.) have been applied for fossil fuel characterisation and kinetics are reviewed. The scientific results presented clearly showed that thermal analysis is a well-established technique used in fossil fuel research area. The literature survey showed that thermal methods were important not only theoretically but also from a practical point of view.

**Keywords:** coal, combustion, crude oil, differential scanning calorimetry, fossil fuels, lignite, oil shale, pyrolysis, thermogravimetry

**Introduction**

In recent years the application of thermal analysis techniques to study the combustion-pyrolysis behaviour and kinetics of fossil fuels has gained a wide acceptance among research workers, which is of exceptional significance for industry and for the economy. The references cited in the review are not meant to be comprehensive compilation of all the thermal analysis methods that have been attempted on fossil fuels; rather the approach is one wherein a particular application is highlighted using typical studies.

Until now much work has been carried out to study the combustion and pyrolysis processes taking place in fossil fuels using thermal analysis techniques. Therefore, the goal of this review is to present the applications of thermal analysis techniques in fossil fuel science.

## Literature survey

### *TG/DTG and DTA studies on coal samples*

Historically, differential thermal analysis (DTA) was the first thermoanalytical tool used in studying coal samples. Much of the work on thermal analysis of coal samples was directed towards correlation between thermal behaviour and rank or towards characterisation of various stages in the carbonisation process.

Rai and Tran [1] conducted a kinetic study on non-catalysed and catalysed coal. In their kinetic model, the apparent activation energy is measured to be a rectilinear function of the extent of reaction to describe the pyrolysis of Hanna coal. For the hydro gasification of char, the apparent activation energy was found to vary as a second-degree polynomial with respect to conversion. The order of reaction was found to be about 0.3 for the pyrolysis step and 0.67 for the hydro gasification step. Ciuryla and Welmer [2] performed ambient-pressure thermogravimetric characterisation (TG/DTG) of four different coals and their chars to obtain fundamental information on pyrolysis, and coal and char reactivity for these materials. Mass loss as a function of temperature was systematically determined for each coal heated in helium at 40 and 160°C min<sup>-1</sup> under various experimental conditions and for its derived char heated in air over a temperature range of 20–1000°C. The results indicate that the temperature of the maximum rate of devolatilization increases heating rate for all coals. Collett and Rund [3] studied the thermogravimetric measurements of mass loss (TG/DTG) accompanying the pyrolysis of four pitches over two ranges of linear heating rates. The data for all samples described by the multiple heating rates methods and activation energies increased with the value of the heating rate. Ratcliffe and Pap [4] has investigated the reactivity of lignite and different ranks of coal samples. In all the coal samples studied, the reaction occurred in two distinct stages. A rapid initial stage was controlled primarily by the devolatilization rate of the coal. The second stage limited the overall rate and was controlled by the surface properties of coal. Gold [5] demonstrated the occurrence of exothermic processes associated with the production of volatile matter in or near the plastic region of the coal samples studied (TG/DTG). He observed that the temperature and magnitude of the exothermic peak was strongly affected by the heating rate, sample mass and particle size. Cumming [6] has developed a method for describing the reactivity or combustibility of solid fuels, such as lignite, bituminous coals and petroleum coke, in terms of a weighed mean apparent activation energy, derived from simultaneous TG/DTG readings on a 20 mg sample heated at a constant rate in a flowing air atmosphere. He proposed that the mean activation energy method be the established method, which involves recording overall temperatures on the burning profile curve. Smith and Neavel [7] carried out coal combustion experiments in the temperature range 25–900°C using air at atmospheric pressure in a derivative thermogravimetric analysis system (TG/DTG). Sixty-six coals high in vitrinite and low in inorganic were examined as part of a coal characterisation program. The rate data were fitted to an Arrhenius equation and plots showed four distinct regions of combustion. Calculated apparent activation energies

were of the correct orders of magnitude to describe combustion regions corresponding to chemical-reaction-controlled as well as diffusion-controlled processes. Smith *et al.* [8] investigated the burning process of different coal samples (TG/DTG), from lignite to black coal, and found that the burning temperature for half of these coal types is linearly dependent on their concentration. Cumming and Mclaughlin [9] applied TG and DTG to a range of samples and obtained proximate analysis results for a total of 14 coal samples of widely different properties. They have also established burning and volatile release profile tests. They suggested that the volatile release profile test might find application in the fields of coking and gasification rather than in combustion, and that it could be the basis of a system for fingerprinting coals. Elder [10] developed a procedure for the automatic proximate analysis (TG/DTG) of solid fossil fuels and related matter. The procedure is tested with coals of varying rank, biomass samples and Devonian oil shales. The simplicity of the technique suggests that it may complement the classical ASTM method and could be used when this latter procedure cannot be employed. Seragaldin and Pan [11] developed a linear relationship between activation energy and heat of reaction (TG/DTG). The effects of alkali metal salts on the decomposition of coal under three different atmospheres (nitrogen, CO<sub>2</sub> and air) are also investigated. The effect of the catalysts on coal conversion and CH<sub>4</sub>, CO<sub>2</sub> and CO emissions are related to observed changes in the activation energy. Morgan and Robertson [12] determined coal-burning profiles by thermogravimetric analysis. They have claimed that kinetic parameters from Arrhenius plots of the profiles cannot readily be related to any specific stage of combustion. However some features of the profiles are clearly related to coal properties, and a correlation exists between unburned carbon loss as predicted from high-temperature oxidation rates and a characteristic temperature of the thermogravimetric profile. This suggested that burning profiles could provide a valuable, rapid laboratory method of ranking coals in terms of their burnout performance. Patel *et al.* [13] measured the rate of combustion of lignite char using thermogravimetry over a range of oxygen concentrations (5–20%) and at temperatures between 325 and 650°C. The activation energy in the chemical rate-controlled zone was 120 kJ mol<sup>-1</sup> and the transition to film diffusion control occurred at 430°C. The Arrhenius plots indicated no region of pore diffusion control. The pyrolysis conditions were found to have a notable influence on the activation energy. Janikowski and Stenberg [14] analysed ten different coals (four lignites, four sub-bituminous and two bituminous) in argon and hydrogen atmospheres using thermogravimetry. Upon heating the coals in an inert atmosphere up to 500°C, 30.8–43.7% mass loss occurs. They have distinguished two temperature regions of increased chemical reactivity: one at 75–118°C and the second at 375–415°C. Morris [15] carried out pyrolysis runs on a low-ash coal and correlated yields of hydrogen and methane as a function of particle size and final temperature, and yields of CO and CO<sub>2</sub> as a function of particle size at a final temperature before decomposition of the carbonates in the mineral matter. Alula *et al.* [16] used TG and DSC to characterise low- and high-temperature coal tar and petroleum pitches and their fractions, thermal methods to the characterisation of pyrolysis coal products. The temperature at which the maximum rate of mass loss is observed and determined, and its variation with the

specific heat and glass transition temperatures was discussed. Crelling *et al.* [17] determined the combustion properties of separated single coal maceral fractions from a rank series of coals and then tried to predict the combustion behaviour of various whole coals on the basis of their maceral composition and rank (DTA). The results of this study indicate that most of the reactivity and combustion profile parameters varied significantly with coal rank. Alonso *et al.* [18] studied the pyrolysis of a number of coal tar and petroleum pitches by means of thermal methods. Acenzathylene was used as a model compound to interpret the results of thermal methods. DTA exothermic and endothermic peaks were assigned to different types of phenomena such as devolatilization, polymerisation, condensation and cracking. It was found that endothermic phenomena are prevalent for binder coal tar pitches. Coil *et al.* [19] developed a dynamic pyrolysis model, which takes into account three different groups of thermal decomposition reactions of coals (TG/DTG). A simple procedure is proposed for determining the kinetic parameters. The kinetic parameters were determined using a differential method and the experimental data obtained at low heating rates. Furthermore, this method allowed the determination of the lowest value of the heating rate at which a single peak will be obtained. Haykiri *et al.* [20] investigated the behaviour of some fossil fuels during thermal treatment. DTA and TG were applied to peat, lignite, bituminous coal, anthracite, oil shale and asphaltite samples under a nitrogen atmosphere, and the results are discussed. They concluded that an increase in the ratio of the volatile matter content of the active matter content of coal causes a decrease in the maximum mass loss rate temperature. Morris [21] carried out pyrolysis runs (TG/DTG) in the temperature range ambient to 900°C and the particle size 38–2360 µm on a low ash coal. Empirical correlations were established for the evaluation rates of hydrogen, carbon monoxide and methane as a function of particle size and instantaneous temperature. The observations suggest that tar deposition is rate determining. The observations for the rate of evaluation suggest that it be governed by several complex reactions of which methanation and secondary cracking of tar are possibilities. Mianowski and Radko [22] developed a method for the evaluation of the temperature range to calculate the kinetic parameters of coal pyrolysis using thermogravimetry. For twelve coal samples of different rank, it is shown that pyrolysis in the temperature range 280–580°C is a first-order process with an activation energy of 78–151 kJ mol<sup>-1</sup>. An iso-kinetic effect is also observed for the coal samples investigated. Solomon and Serai [23] used the most popular technique (solvent swelling ratio) for cross-linking reactions in coal and char, and this technique has been used to determine cross-link density changes during pyrolysis and liquefaction. The results from pyrolysis studies at heating rates between 0.5 and 100°C min<sup>-1</sup> show that cross-linking is rank-dependent, occurring in lignites at lower temperatures than in bituminous coals. Nosyrev *et al.* [24] studied the influence on its thermal behaviour of the structural modifications afforded to a bituminous coal by several chemical treatments by thermogravimetry. The results were discussed in relation to the structural information already obtained by infrared spectroscopy and with the rheological properties characterised by thermo mechanical analysis. Kök [25] investigated the thermal behaviour of lignite using TG/DTG, high-pressure thermogravimetry

(HPTG) and combustion cell experiments. Different models (Arrhenius, Coats and Redfern, Fassihi and Brigham) were used to obtain kinetic parameters and the results are discussed. Kök *et al.* [26] studied the effect of particle size on the combustion properties of coal sample. Non-isothermal thermogravimetry experiments were carried out for twelve different size fractions on the coal sample. TG/DTG experiments were performed from ambient to 900°C in air atmosphere and the data were analysed using an Arrhenius type reaction model assuming a first-order reaction. Kinetic parameters of the samples were determined and the results are discussed. Kök *et al.* [27] studied the effect of particle size on coal pyrolysis by thermogravimetry. Different fractions of coal showed differences in TG/DTG curves, peak temperatures and residue values. The Arrhenius model is applied to determine the kinetic parameters from TG/DTG curves and the results are discussed. Huang *et al.* [28] investigated a wide range of coal ranks from lignite to anthracite using thermogravimetric analysis. The derivative peak maximum for volatile matter evolution shows a strong correlation with vitrinite reflectance, thereby providing a convenient measure of degree of coalification (coal rank) without requiring the equipment of and more time-consuming petrographic analysis. *T*-max by the rock eval method also shows a positive correlation with vitrinite reflectance. TG also reproduces the components of the proximate analysis of coal. Liu *et al.* [29] investigated the combustion behaviour of coal dust by means of thermogravimetry. The reaction fraction alpha can be obtained from isothermal TG/DTG data. The mechanism of nucleation and nuclei growth is determined as a controlling step of the coal dust combustion reaction by the correlation coefficient of the regression, and the kinetic equation of the coal dust combustion reaction has been established. Pranda *et al.* [30] performed combustion experiments in air using TG/DTA analysis, which served for ignition temperature and kinetics data determination. Fly-ash carbon was treated with carbonates and hydroxides. The ignition temperature dependence on alkali metal salt concentration was investigated. Results showed that the ignition temperature decreased for treated samples. The activation energy of impregnated samples decreased. Kök [31] studied the effect of particle size on the oxidation mechanisms of lignites. Non-isothermal thermogravimetry experiments were performed for twelve different size fractions. Data obtained from TG/DTG experiments are converted into dimensionless size vs. dimensionless time to show the progress of oxidation mechanisms of lignites. It was found that lignites show linear behaviour at elevated temperatures, which justifies the assumption that chemical reaction is the controlling step. Boiko [32] discussed the methods for the complex thermoanalysis of solid fuels. The following processes were studied: moisture evaporation, emission of volatile products, and reaction of non-volatile fuel residue within the oxygen in air. The results of the work can be used in mathematical simulation of processes for the coal processing using power technology. Benfell *et al.* [33] used thermogravimetry for characterising the effects of rank and maceral variations of coal combustion behaviour. These coals showed an increase in char burnout temperature with rank for both dull, inertinite-rich and bright, vitrinite-rich coals. It was observed that the maximum rates of combustion for dull coals are lower than their bright counterparts, with the difference between the two varying with rank.

Ozbas *et al.* [34] presented the results of a study on the combustion characteristics of lignite before and after the cleaning process. Non-isothermal thermogravimetry experiments were carried out for four different size fractions. TG/DTG curves revealed three reaction regions as; evaporation of moisture in the coal, primary reaction region and decomposition of mineral matter in the lignite. Mayoral *et al.* [35] reported the experimental optimisation by the simplex method of the proximate analysis of coal and biomass by thermal analysis (TG/DTG). Heating rate, final temperature, holding time, gas flow rate and sample size were the control variables. The relative accuracy of the method was demonstrated by determination of the volatile matter contents of a number of coals. Kök [36] analysed the combustion curves of seventeen lignite samples using thermogravimetry. A comparative analysis was performed considering the relationship between peak temperature, burnout temperature, moisture content, ash, volatile matter, fixed carbon and calorific values of the samples studied. Iordanidis *et al.* [37] carried out thermogravimetry (TG and DTA) experiments for seven lignite samples. The samples were chosen to represent the vertical distribution of the lignite beds in the entire deposit. The burning profiles of the samples studied, combined with proximate analysis and calorimetry results, contribute to a clearer identification of lignite structure and a better understanding of the coalification process. Seven thermal effects were distinguished and a good correlation between the results of proximate and calorimetry analyses and DTA and TG data is noticed. Alonso *et al.* [38] investigated the pyrolysis and combustion behaviour of a set of eleven coals with different ranks and maceral composition by thermogravimetry. Results showed that the pyrolysis curves of coals do not match at all any specific features of the corresponding combustion profiles, and that the temperature of initiation of both processes are very different in the low-rank end, to become similar only for coal ranks of similar vitrinite reflectance and above. Várhegyi *et al.* [39] developed a least squares criteria for the kinetic evaluation of thermal analysis experiments. They discussed several evaluation techniques for handling the non-statistical errors during the least squares evaluation of experimental series. The methods are illustrated by the evaluation of oxidative thermogravimetric experiments of a lignite.

#### *DSC, TG-MS-FTIR studies on coal samples*

Mahajan and Tomita [40] reported differential scanning calorimetry curves for 12 coals of various ranks in a helium atmosphere at 5.6 MPa and at temperatures up to 580°C. They concluded that the thermal effects during the pyrolysis of coals ranging in rank from anthracite to bituminous coals were endothermic. Exothermic heats were observed only in the case of sub-bituminous coals or lignites. The net thermal effects were found to be strongly rank-dependent. Rosenvald and Dubow [41] analysed the pyrolysis of 21 bituminous coal samples by DSC. They have distinguished three regions of endothermic activity in differential scanning calorimetry curves. The first peak (25–150°C) corresponds to a loss of moisture: the second, very broad endotherm peaking in the range 400–450°C corresponds to the devolatilization of organic matter and above 550°C probably corresponds to cracking and coking pro-

cesses subsequent to the pyrolysis step. Butler and Soulard [42] investigated the specific heats ( $C_p$ ) of bituminous and sub-bituminous coals in the temperature range 25–325°C by DSC. Good agreement was obtained with the values for the specific heats of glass and graphites in literature, and it was established that the specific heats were not dependent on the degree of diminution of these materials. Specific heats of coal samples were found to depend upon the mesh size, temperature, rank, moisture content and whether the coal powder was wet- or dry-screened. Richardson [43] measured the specific heats of a range of coals, cokes and ashes using differential scanning calorimetry. He observed a rapid increase of specific heat with content of volatile matter in the region 0–10 mass% followed by only mild increases at high concentrations. Elder and Harris [44] investigated the thermal characteristics of Kentucky bituminous coals undergoing pyrolysis in an inert atmosphere at three different heating rates and determined the specific heats of the coals by DSC. The specific heats of the dry coals lie in the range 1.21–1.47 J g<sup>-1</sup> K<sup>-1</sup>. The exothermic heat flow from 300 to 550°C where the major mass loss occurs, has been associated with the primary carbonisation process and the development of the plastic state, and the onset of secondary gasification, which is responsible for coke formation, was established. Starzewski and Zielenkiewicz [45] investigated the influence of the inert gases helium and argon on the thermal properties of coal using DSC. The coals studied were high-volatiles bituminous coal and anthracite. It has been stated that the heat capacity of coal is strongly influenced by helium. This phenomenon is especially distinct for high-volatiles bituminous coal. Richardson [46] measured the specific heats of a range of coals, cokes and ashes from 25 to 750°C using DSC under pyrolysis conditions. A rapid increase of specific heat with the content of volatile matter in the region 0–10 mass% was followed by only mild increases at higher concentrations. A general equation is given expressing the heat capacity of a coal in terms of proximate composition and temperature, and provides a simple and accurate method of assessing enthalpy changes up to 325°C. Warne [47] discussed the application of thermal analysis (TA) in the earth sciences particularly for the assessment of coal, its constituents and products. A growing number of TA methods have been involved culminating in the use of thermomagnetometry (TM), high temperature differential scanning calorimetry and the wide ranging new method of proton magnetic resonance thermal analysis (PMRTA). In addition to the previously perfected and now widely utilised techniques of TA, ‘simultaneous thermal analysis’ and ‘variable atmosphere thermal analysis’ have proved invaluable particularly the latter where the furnace atmosphere conditions may be pre-selected, controlled and ultimately even changed repeatedly during individual TA runs. Ceylan *et al.* [48] investigated the kinetics of non-isothermal pyrolysis of raw, de-mineralised or oxidised lignites by thermogravimetry, differential thermal analysis and differential scanning calorimetry. The experiments were carried out in an inert and air atmosphere. The mass loss data indicate that pyrolysis characteristics of the lignites and the prevailing kinetic mechanisms vary depending on temperature. The mass loss rates show essentially two regimes and the major mass loss occurs in the range of 300–650°C. It was found that DTA and DSC data gave similar values for the overall reaction order and activation energy. Zoller *et*

*al.* [49] studied the volatile matter evolved during pyrolysis of different rank coals by thermogravimetry and photoionization mass spectrometry (TG-PI-MS). The composition of the TG effluent revealed several significant trends with coal rank. It was observed that the analysis of the raw coal, extracted material and coal residue remaining after solvent extraction produced very similar mass spectral. The results from these analysis suggest that volatile matter, like coal itself, consists of compounds with a range of molecular masses but with similar molecular structures. Pitkanen *et al.* [50] studied various fuels as coal, peat, wood chips, and bark with FTIR spectrometry combined with TG. The gases evolved in a TG analyser were transferred to the FTIR via a heated teflon line. The spectra and thermoanalytical curves indicated that the major gases evolved were carbon dioxide and water, while there were many minor gases, e.g. carbon monoxide, methane, ethane, methanol, ethanol, formic acid, acetic acid and formaldehyde. Takanohashi *et al.* [51] applied differential scanning calorimetry to study the extraction residues of coals giving different extraction yields. For the residues with extraction yields lower than 30 mass%, an endothermic peak similar to that given by the raw coal was observed around 300°C. This endothermic peak disappeared on the second and third scans, indicating that the peak is due to irreversible structural changes in coal. The reason for these endothermic peaks was discussed from the relationship among the extraction, swelling, and structural changes of coals. Garcia *et al.* [52] measured the non-isothermal oxidation enthalpies for three coals, which have been weathered under ambient conditions. It was found that although the total oxidation enthalpies decreased with increasing oxidation, the decrease was not systematic. It was noted that the onset temperature of oxidation increased with oxidation in a more systematic way and also increased with increasing coal rank. It was therefore proposed that the onset temperatures were a better indicator of the propensity of the coals to oxidation. Xie and Pan [53] analysed the thermal characterisation of materials using evolved gas analysis. TG/FTIR, TG/MS and pyrolysis/GC-MS systems and their applications in the study of several materials are discussed, including the analysis of the degradation mechanisms of originally modified clays, polymers and coal blends.

#### *DSC, TG/DTG, DTA and TG-GC-FTIR studies on crude oil samples*

Differential thermal analysis was the first thermoanalytical tool used in crude oil characterisation. Much of the work on thermal analysis of crude oils was directed towards correlation between thermal behaviour of the samples and kinetic studies. Effect of different metallic additives on the combustion properties of crude oils is also studied.

Burger and Sahuquet [54] used DTA to illustrate the catalytic effect of some metallic derivatives and to investigate how the properties of both oil and porous media influence crude oil combustion. Three successive oxidation regions were observed in the DTA curves, namely low-temperature partial oxidation, combustion of crude oil fractions and finally, coke combustion. Bae [55] investigated the thermo-oxidative behaviour and fuel-forming properties of various crude oils using thermogravimetry.



The results indicated that oils can be classified according to their oxidation characteristics. No complete correlation could be established between viscosity, composition or density of the crude with the thermo-oxidative characteristics of the oil. Drici and Vossoughi [56] applied DSC and TG/DTG to crude oil combustion in the presence and absence of metal oxides. Vanadium, nickel and ferric oxides behaved similarly in enhancing the endothermic reactions. In the presence of a large surface area such as on silica, the surface reactions are predominant and unaffected by the small amount of metal oxide present. Vossoughi and Bartlett [57] has developed a kinetic model of the in situ combustion process from data obtained from thermogravimetry and differential scanning calorimetry. They used the kinetic model to predict fuel deposition and combustion rate in a combustion tube. Good agreement was obtained between predicted and observed fuel deposition and combustion rate in a combustion tube. Vossoughi [58] has used TG/DTG and DSC techniques to study the effect of clay and surface area on the combustion of selected oil samples. The results indicate that there was a significant reduction in the activation energy of the combustion reaction regardless of the chemical composition of additives. Moreover, the low-temperature oxidation of the oil and probably the coke deposition were strongly affected by the specific surface area of the solid matrix. Yoshiki and Phillips [59] examined the thermo-oxidative and thermal cracking reactions of Athabasca bitumen qualitatively and quantitatively using differential thermal analysis. Reaction kinetics of low-temperature oxidation and high-temperature cracking were determined. The effects of atmosphere, pressure, heating rate and support material on the thermal reactions of bitumen were studied. They have found that low linear heating rates ( $2.8^{\circ}\text{C min}^{-1}$ ) favoured low-temperature oxidative addition and fission reactions. Verkocý and Kamal [60] performed thermogravimetry and pressurised differential scanning calorimetry (PDSC) investigations on Saskatchewan heavy oils collected from wells under primary, steam flood and fire-flood production, and on cores. They have estimated kinetic and thermochemical data for thermolysis, low-temperature oxidation and combustion reaction rates, which were non-linearly dependent on the heating rate. Kamal and Verkocý [61] used TG/DTG and DSC on two Lloydminster regions, heavy-oil cores, and extracted oils and mineral matter. TG/DTG and DSC curves of two Lloydminster region cores and extracted oils obtained in helium and air atmospheres demonstrated at least three groups of chemical reactions occurring in three temperature regions. Reactions in zone 1 are attributed to evaporation, distillation, thermolysis, and low-temperature oxidation (LTO), in zone 2 to distillation and thermal alteration of minerals, LTO, and combustion, and in zone 3 and/or 4 to pyrolysis, coking, polymerisation, mineral matter decomposition and combustion. Ranjbar and Pusch [62] studied the effect of the oil composition, characterized on the basis of light hydrocarbon, resin and asphaltene contents, on the pyrolysis kinetics of the oil and the combustion kinetics of the fuel by thermogravimetry and differential scanning calorimetry. The results of their investigations showed that the colloidal composition of oil as well as the transfer-ability and heat transfer characteristics of the pyrolysis medium has a pronounced influence on fuel formation and composition. Ahmed and Saleem [63] investigated the asphaltenes precipitated from Arabian crude oils by thermo-

gravimetry and pyrolysis-GC analysis at 350 and 520°C. Under severe pyrolysis conditions (520°C), 98–100% of asphaltenes are converted to the products. The evaluation of methane and other normal alkanes from all the asphaltenes under mild pyrolysis conditions indicates that these asphaltenes contain thermally labile alkyl groups on the periphery of these asphaltenes. The loss of nitrogen from the asphaltenes during pyrolysis remained low (1–6 mass%), whereas the losses of oxygen and sulphur ranged from 58 to 74 and 10 to 29 mass%, respectively. Ranjbar [64] investigated the influence of reservoir rock composition on the pyrolysis and combustion behaviour of crude oils in porous media. Pyrolysis and combustion tests were performed to examine how clays affect the amount of fuel and its reactivity. From the experimental results, he concluded that clay minerals present in the matrix enhance fuel deposition during the pyrolysis process and also catalyse the oxidation of fuel. Kök and Okandan [65] analysed the combustion properties of crude oil-lignite mixtures by DSC. The effect of heating rate was also studied and higher reaction temperatures and heat flow rates were observed with increasing heating rate. The specific heat of samples was examined in the temperature range 20–660°C. The specific heat of samples increased continuously with increasing temperature until the decomposition temperature was reached. Activation energies of the mixtures were also calculated and were found to vary between 66–131 kJ mol<sup>-1</sup>. Kök [66] characterized the pyrolysis and combustion properties of two heavy crude oils. On combustion in air, three different reaction regions were identified, known as low-temperature oxidation, fuel deposition and high-temperature oxidation. DSC-TG/DTG curves have also been used to determine the heat values and reaction parameters of crude oil. Kinetic data were obtained from the high-temperature oxidation region from the DSC and DTG curves. Higher activation energy values were found as API gravity of the crude oil decreased. Kopsch [67] determined the glass transition temperature of petroleum asphaltenes using DSC. From this temperature a hypothetical melting temperature of the asphaltenes can be calculated as falling within the range of pyrolysis temperature of asphaltenes. The glass transition in polymers is a kinetically controlled reaction, which can be described with the help of activation energy. They have also found a relationship between the glass transition temperature and the melting temperature of the petroleum asphaltenes studied. Lukyaa *et al.* [68] used pressurised differential scanning calorimetry to study the effects of sand particle size, pressure and oxygen partial pressure on the heat evolution during the combustion of North Sea crude-sand mixtures. They observed that decreasing particle size of the sand and increased pressure the extent of low-temperatures oxidation and thus favoured fuel lay-down. Kök *et al.* [69] used pressurized differential scanning calorimetry to obtain information on the combustion characteristics of crude oils and their mixtures in two chemically different matrix materials, sand and limestone. Crude oil and sand/limestone mixtures were prepared to give a composition of 10 mass% crude oil in matrix. The PDSC curve clearly demonstrates two distinct transitional stages, namely combustion of liquid hydrocarbons and combustion of coke. The kinetic part of this research is concerned with only one peak namely the coke combustion. Two different kinetic models analysed kinetic data and the results are discussed. Kök and Karacan [70] presented the results of an

experimental study on the determination of pyrolysis behaviour and kinetics of six crude oils by differential scanning calorimetry and thermogravimetry. Crude oil pyrolysis indicated two main temperature ranges where loss of mass was observed. The first region between ambient and to 400°C was distillation. The second region between 400 and 600°C was visbreaking and thermal breaking. It was observed that as crude oil gets heavier cracking activation energy increases. Activation energy of cracking also shows a general trend with asphaltene content. Di Lalla and Kosinski [71] developed a new methodology using TGF/FTIR to study the low temperature treatment of waste lubricating oils. It was found that the majority of the process in terms of mass loss and gas-phase evolution was over by 650°C, and thus the remainder of the sample heating was accomplished at a rate of 5°C min<sup>-1</sup>. The information gathered was used to understand and explain the evolution of the waste oil from initial liquid state to final solid ash state. Laux *et al.* [72] investigated an atmospheric residue, a vacuum residue, a visbreaking residue the maltene fractions of the residues, mixture of the atmospheric residue with the vacuum residue and the residue from the supercritical extraction of the vacuum residue as well as the residues mixed with dispersing agents by thermogravimetry at three different heating rates. It was found that besides the content of colloid disperse phase its stability has a significant influence on the properties of the residues, especially on the evaporation enthalpy. The stability of residues was investigated by the flocculation point determination. Thermogravimetry proves to be an effective method for the determination of important parameters of processing of crude oil residues considering the influence of the colloidal character of these complex mixtures. Goncalves *et al.* [73] investigated the thermal behaviour of asphaltenes from crude oil using thermal analysis techniques (TG-DTA/GC/MS). The approach involves kinetic studies of the thermal decomposition of asphaltenes under controlled conditions by thermogravimetry, characterization of volatile fractions by TG and DTA coupled with gas chromatography/mass spectrometry and by gas chromatography/mass spectrometry in the volatile recovered. The coke formed was also studied after being decomposed into smaller molecules using selective oxidation. Kök and Iscan [74] applied differential scanning calorimetry to crude oil combustion in the presence and absence of metal chlorides. It was observed that in the presence of smaller ratios of metallic additives, the surface reactions were predominant and the catalyst did not affect the reactions much. Three different reaction regions were identified as low temperature oxidation, fuel deposition and high temperature oxidation in all the samples studied. Kök and Keskin [75] investigated the thermal characteristics and kinetics of three crude oils using thermogravimetry. In combustion with air, three distinct reaction regions were identified in all crude oil samples studied, known as low temperature oxidation, fuel deposition and high temperature oxidation. A computer program was developed for automatically processing the data to estimate the reaction parameters.

*DSC, TG/DTG, DTA and TG-GC-FTIR studies on oil shale samples*

Much of the work on thermal analysis of oil shale samples was directed towards characterisation, pyrolysis-combustion kinetic analysis.

Shih and Sohn [76] used non-isothermal TG with a variety of heating rates to the determination of kinetics parameters for Green River oil shale pyrolysis. Four different methods were employed for kinetics analysis and the results appear to be in fair agreement. The same group has employed non-isothermal TG for studying the oxidation kinetics of oil shale char under conditions in which diffusion and mass transfer effects were claimed to be unimportant. Rejashwar [77] studied the pyrolysis kinetics of the thermal decomposition of Green River oil shale kerogen by non-isothermal thermogravimetry. He critically reviewed the factors influencing kinetic data such as sample order geometry, heating rate and atmosphere. He analysed the mass loss data by direct Arrhenius, Coats–Redfern and Freeman–Carroll techniques. Sweeney [78] obtained DTA curves for selected micaceous soil/clays from the Eastern Caribbean over the temperature range 25–1150°C. The curves run under N<sub>2</sub> were used to identify the clay minerals present. Supporting evidence on the clay minerals present was found from X-ray crystallographic techniques. They have obtained a marked similarity between the curves of the virgin soils analysed under nitrogen gas and the clays from which the organic constituents had been analytically degraded. Earnest [79] analysed the thermal behaviour of Green River oil shale in a dynamic nitrogen atmosphere with TG and DTG and compared it with that in retorting processes. Using the results of this study, the pyrolysis onset temperatures and the temperatures at the maximum pyrolysis rate were related to the type of organic maceral components of the oil shale specimen. Thakur and Nuttall [80] studied the pyrolysis kinetics of the thermal decomposition of Moroccan oil shale by isothermal and non-isothermal thermogravimetry. The combined use of non-isothermal and isothermal TG measurements has shown that the thermal decomposition of Moroccan oil shale involves two consecutive reactions with bitumen as an intermediate. Both reactions follow first-order kinetics. Among the three models used, the Antony–Howard model yields lower deviation and thus provides a better fit of the data. Skala *et al.* [81] have investigated the pyrolysis kinetics of oil shales under non-isothermal conditions using thermal methods. The results obtained were incorporated into the multi-step kinetic model which was adjusted according to the specific properties of particular oil shale samples and tested by comparison of the experimental and simulated TG, DTG and DSC curves. The modelling procedure developed was found to be useful in modelling the pyrolysis of other oil shales of the same kerogen type. Skala and Sokic [82] developed a kinetic expression commonly used in the thermal analysis of oil shale pyrolysis. This was derived on the basis of a simple first-order kinetic equation of kerogen decomposition. The obtained results show that the largest activation energies were detected by using isothermal TG, while combined non-isothermal and isothermal TG gave the smallest values. In all the examined samples and TG analyses performed, there was an increase in the activation energy with increased content of paraffinic structures in the oil shale. Burnham [83] showed how chemical kinetics influences

the design and operation of different processes for different types of oil shales. Reaction kinetics is presented for organic pyrolysis. He also reviewed briefly the pyrolysis results with the intention of drawing comparisons between open, high-pressure and hydrous pyrolysis. Empirically, the degree of severity of pyrolysis required to form a volatile product in open pyrolysis is similar to that required to form an expelled oil phase in hydrous pyrolysis. Lillack and Schwochau [84] performed ion-isothermal pyrolysis experiments on an immature oil shale sample. Evaluation of the experimental evolution profiles with a kinetic model yielded more kinetic parameters. Fainberg and Hetsroni [85] studied secondary pyrolysis of products of Israeli oil shale processing in a two-stage bench-scale unit. The gas and oil vapours generated from the primary pyrolysis were sent to the converter for the secondary pyrolysis at temperatures of 650–820°C. The oil yield on kerogen decreased from 35.3% at the pyrolysis temperature of 500°C to 15.4% at 820°C. The gas yield increased in the same temperature range from 10.7 to 25.5%. The yields of hydrogen, methane, ethylene, and carbon monoxide increased with temperature, whereas yields of alkanes decreased. The secondary pyrolysis enables us to simplify substantially the composition of the primary shale oil. Kök and Pamir [86] used differential scanning calorimeter to determine the combustion kinetics of oil shale samples by ASTM method. It was observed that higher heating rates resulted in higher reaction temperatures and higher heat of reactions. Distinguishing peaks shifted to higher temperatures with an increase in heating rate. Activation energy values were found in the range of 131.8–185.3 kJ mol<sup>-1</sup>. Lisboa and Watkinson [87] used standard thermogravimetric apparatuses for the study of the chemical kinetics of oil shale pyrolysis and combustion, such as controlled temperature and simultaneous weighing of the sample. The thermogravimetric analyses must be carried out in such conditions that the observed reaction rate is identical to the rate of the chemical kinetics. This study investigated the effects of key parameters, which could affect this identity, such as: the gas flow rate, the gas purity, the gas nature, the particle sizes and sample sizes. Jaber and Probert [88] studied two oil shale samples non-isothermally using a thermogravimetric analyser. The controlling parameters studied were the final temperature and influence of particle size as well as the heating rate employed during the process of thermal degradation of the oil shale sample. The integral method was used in the analysis of mass loss data to determine the pyrolysis and gasification kinetics. Gasification and pyrolysis of the investigated shales complied with first-order kinetics. The activation energy decreased slightly as the shale-particle size reduced. Lisboa and Watkinson [89] studied the chemical kinetics of oil shale pyrolysis and combustion with thermogravimetric apparatus. This study investigated the effects of key parameters, which could effect the gas flow rate, the gas purity, the gas nature, and the particle size and sample sizes. Kök *et al.* [90] used pressurized differential scanning calorimeter to obtain information on the pyrolysis and combustion characteristics of oil shales at different pressures (100–400 psi). Two distinct peaks were identified in combustion experiments known as low temperature oxidation (LTO) and high temperature oxidation (HTO) reaction regions. The pyrolysis process of all oil shale samples showed one exothermic effect on each total pressure studied. Kinetic data were

analysed and the results are discussed. Karabakan and Yurum [91] investigated the effect of mineral matrix of oil shales and air diffusion on the conversion of organic material in oxidation reactions. The overall reaction orders from the kinetic analysis were found to be pseudo-first-order. The magnitude of the activation energies of oxidation reactions at equal heating rates changed. It was found that the rate of reaction depends on the rate of transport of the gas into the zone of reaction by diffusion. It was also observed that the diffusion of oxygen into the organic matrix was the major resistance controlling the rate of oxidation reactions. Gersten *et al.* [92] investigated the thermal decomposition behaviour of poly(propylene), oil shale and a 1:3 mixture of the two in a thermogravimetric analyser reaction system in an argon atmosphere. Experiments were conducted at three heating rates in the temperature range of 30–900°C. The results indicate that the characteristics of the process depend on the heating rate, and the poly(propylene) acts as a catalyst in the degradation of oil shale in the mixture. Berkovich *et al.* [93] presented a novel technique to the thermal characterization of oil shale. This approach involves the separation of the unique components of oil shale, the kerogen and the clay minerals, using chemical and physical techniques. The heat capacity and enthalpy changes for the kerogen and clay minerals were measured using non-isothermal modulated DSC from 25 to 500°C. Enthalpy data for dehydration and pyrolysis of kerogen were also determined. Jaber and Probert [94] pyrolysed oil shale samples using a thermogravimetric analyser. The controlling parameters studied were the final pyrolysis temperature and the influence of the heating rate as well as type of purge gas employed on the process of thermal degradation of the shale sample. The integral method was used in the analysis of TG data in order to determine the pyrolysis kinetics. It was observed that the magnitude of the total mass loss was mainly dependent on the final temperature, as well as, to a lesser extent, on the heating rate employed. Williams and Ahmad [95] pyrolysed oil shale samples in a thermogravimetric analyser in relation to heating rate and temperature using non-isothermal and isothermal analysis respectively. The main region of mass loss corresponding to hydrocarbon oil and gas release was between 200–620°C and at higher temperatures significant mass loss was attributed to carbonate decomposition. It was found that for the oil shale samples analysed, increasing the heating rate shifted the reaction to higher temperatures. The kinetic data were analysed using Arrhenius and Coats and Redfern methods. There was no clear relationship between activation energy and heating rate. Kök and Pamir [96] determined the thermal characteristics and kinetic parameters of oil shale samples by TG and DTG at non-isothermal heating conditions both for pyrolysis and combustion processes. A general computer program was developed and the methods are compared with regard to their accuracy and the ease of interpretation of the kinetics of thermal decomposition. Activation energies of the oil shale samples were determined by five different methods and the results are discussed. Williams and Ahmad [97] investigated the pyrolysis behaviour of two oil shales in a thermogravimetry and fixed bed reactor to determine the influence of temperature and heating rate on the thermal degradation of the samples. It was found that for the oil shale samples analysed in TG/DTG, increasing the heating rate shifted the reactions to higher temperatures. The main region of mass

loss corresponding to hydrocarbon oil and gas release was between 20–620°C, and at higher temperatures, significant mass loss was attributed to carbonate decomposition. Torrento and Galan [98] studied the kinetics of thermal decomposition of oil shale using thermogravimetry. It was observed that the rate of thermal decomposition of oil shale can be suitably described by overall first-order kinetics. No mass and heat transfer resistance was observed for the different particle sizes studied. Jaber and Mohsen [99] investigated the drying kinetics of two oil shales from different deposits over a temperature range of 70–150°C in thermogravimetry under direct insulation. The mass loss and drying rates of the samples were determined gravimetrically. It has been observed that drying rate falls off at a critical temperature (120°C) and approaches zero beyond this temperature.

## Conclusions

A survey of the literature reveals that thermal methods are finding an increasing application in the study of fossil fuels, and that thermal analysis techniques have been applied very successfully to studies of the interaction of these fossil fuels with nitrogen and with other gases such as air and oxygen. Use of these techniques has considerable significance in terms of the determination of the changes in properties such as composition, decomposition characteristics, calorific effects, kinetics, proximate analysis, etc. The literature survey showed that thermal methods were important not only theoretically but also from a practical point of view.

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