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RECENT DEVELOPMENTS IN THE APPLICATION OF THERMAL ANALYSIS TECHNIQUES IN FOSSIL FUELS

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In this review, application of thermal analysis techniques (differential scanning calorimetry, thermogravimetry, differential thermal analysis, etc.) for fossil fuel characterization and kinetics are reviewed between 2001 and 2006. The results presented clearly showed that thermal analysis applications are well-established techniques used in fossil fuel research area.

Keywords: *calorimetry, coal, combustion, crude oil, fossil fuels, kinetics, lignite, oil shale, pyrolysis, thermal analysis, thermogravimetry*

Introduction

Thermal analysis characterizes the physical and chemical properties of substances, depending on the temperature at a defined heating rate (dynamic measurement) or on the time at a constant temperature (static measurement). Techniques developed to continuously monitor physical or chemical changes of a sample which occur as the temperature of a sample is increased or decreased. Thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are the principal thermoanalytical methods.

Literature review

In recent years, the application of thermal analysis techniques to study the combustion-pyrolysis behavior and kinetics of fossil fuels has gained a wide acceptance among research workers.

Application of thermal analysis techniques on coal, lignite and asphaltite samples

Historically, differential thermal analysis (DTA) was the first thermo-analytical tool used in studying coal and lignite samples. Mayoral *et al.* [1] studied the proximate analysis of coal and biomass by thermal analysis techniques. 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 [2] analyzed the combustion curves of seventeen lignite samples using thermogravimetry (TG). 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 and the results are discussed. Iordanidis *et al.* [3] carried out thermal analysis (TG-DTA) experiments for seven lignite samples where the burning profiles of the samples are studied considering the proximate analysis and calorimetry results. Different thermal effects were distinguished and a good correlation between the results of proximate and calorimetry analyses and the DTA and TG data is noticed. Alonso *et al.* [4] investigated the pyrolysis and combustion behavior of a set of coals with different ranks and maceral composition by TG. Results showed that the pyrolysis curves of the coals do not match at all with any specific feature 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.* [5] developed least squares criteria for the kinetic evaluation of thermal analysis experiments. They discussed several evaluation techniques for the handling of the non-statistical errors during the least squares evaluation of experimental series. The methods are illustrated by the evaluation of oxidative thermogravimetric experiments of lignite. Mayoral *et al.* [6] reported the experimental optimization by the simplex method of the proximate analysis of coal and biomass by TG. Heating rate, final temperature, holding time, air flow rate and sample size were the control variables. The response function used was chosen to minimize the difference in percentage of volatile matter with the ASTM characterization. The relative accuracy of the method was demonstrated by determination of the volatile matter contents of a number of coals in parallel

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with the ASTM certified method. It was observed that the method is successfully used with biomass samples. Xie and Pan [7] used TG coupled with Fourier transform infrared (FTIR) spectroscopy (TG/FTIR), TG coupled with mass spectrometry (MS) and TG coupled with GC/MS for structural identification of compounds evolving during thermal processes. It was concluded that evolved gas analysis (EGA) techniques allow evaluating the chemical pathway of the degradation reaction by determining the decomposition products including the analysis of the degradation mechanisms of organically modified clays, polymers, and coal blends. Altun *et al.* [8, 9] analyzed the combustion properties of the lignite and different binders were analyzed by TG/DTG.

Molasses, carboxyl methylcellulose (CMC), sulphide liquor, heavy crude oil, sodium silicate, cornstarch, lime, peridur, and bentonite, cement poly-(vinyl acetate) were used as binders. It was observed that molasses and CMC decreased the residue content at the end of the combustion period, whereas, heavy crude oil, sulphide liquor and corn starch increased the calorific values of the samples. Two different kinetic models (Arrhenius and Coats–Redfern) were used to determine the activation energies of the samples studied. It was observed that molasses, CMC, heavy crude oil, peridur, bentonite and poly(acetate) decreased the activation energy of the coal sample, whereas, all other binders increased the activation energy of the coal sample. Kök and Keskin [10] determined the calorific values of coals of different origin by thermal analysis techniques (TG-DTA). The calorific values, those obtained by thermal analysis are compared with an adiabatic bomb calorimeter by the standard ASTM method, and the results are discussed. Kök [11] investigated the thermal behavior of coal samples using simultaneous thermogravimetry (TG/DTG) and DTA methods. Upon heating the coals in an inert atmosphere up to 800°C, 31.4–43.8% mass loss occurs. The two temperature regions of increased chemical reactivity are evident in the coal samples studied.

Kinetic analysis of the samples was determined using two different methods, and the results are discussed. Ozbas *et al.* [12] used TG/DTG to determine the kinetic analysis of different coals and effect of cleaning process on kinetic parameters of raw and cleaned coal samples. Kinetic parameters of the samples were determined using Arrhenius and Coats–Redfern kinetic models and the results are discussed. Ozbas *et al.* [13] studied the combustion characteristics of three different coals with thermal analysis techniques such as differential scanning calorimetry (DSC) and TG/DTG. Lime was added to these coals in concentrations of 3, 7 and 10 mass% to investigate the change in combustible sulfur content and sulfur in ash. It was observed that lime has a positive effect on sulfur emission. Kinetic analysis was also performed to see the effect of lime addition on combustion properties and reaction parameters of the coal samples studied. Kök [14] studied the coal pyrolysis by TG/DTG. During the pyrolysis of the coal samples studied, gradual and continuous mass loss over the entire temperature range was observed. The mass loss below 210°C is related to the removal of moisture. The subsequent pyrolysis process as revealed by the corresponding DTG peak that is related to primary devolatilization, during which carbon, hydrogen, and oxygen compounds are released. Arrhenius-type kinetic model was used to determine the kinetic parameters and the results are discussed. Ozbas *et al.* [15] determined the combustion behavior and kinetic analysis of raw and cleaned coal samples of different size fractions by DSC. DSC curves of the three coal samples showed two reaction regions. The first reaction region was due to moisture loss (endothermic) and observed in the temperature range of ambient to 150°C. The second region was the exothermic region due to the combustion and observed in the temperature range of 150 to 600°C. Kinetic parameters of the samples were determined using different kinetic models and the results are discussed. Mendez *et al.* [16] examined the burning characteristics of coal samples at programmed temperature in a thermo balance to classify them. Combustion profiles are affected by different coal properties and characteristics such as particle size, rank, maceral composition and mineral matter content. The favorable effect of mineral matter content on the reactivity has shown to be related to the maceral size within the density fractions and the intimate association organic/mineral matter that favors the diffusion of the reacting gas. Avid *et al.* [17] determined the influence of temperature, heating rate and purge gas employed on the thermal degradation of the coal sample. The heating rates investigated in the TG were 10–50 K min^{-1} to final temperature of 1000°C. N_2 or CO_2 were employed as well as type of purge gas on the process of thermal degradation of the coal sample. The coal was also investigated in a fixed bed reactor to determine the influence of temperature and heating rate of the pyrolysis on the yield of products and composition of the gases evolved. Li *et al.* [18] investigated the thermal behavior of Chinese coals of different ranks by means of thermal analysis/mass spectrometry (TA/MS). The experiments were carried out in a synthetic air atmosphere (20% oxygen+80% nitrogen) with a flow rate of 150 m min^{-1}, and the samples were heated from 40 up to 1200°C at a constant heating rate of 10 K min^{-1}. The volatile products and their evolution profiles against the temperature during the combustion were identified through the on-line recorded mass spectra.

The results revealed that the whole combustion procedure could be broadly divided into four phases and the temperature of the maximum mass loss rate shifted to lower temperatures as the coal rank decreased. Barriocanal *et al.* [19] studied the bituminous coals of different rank in a nitrogen atmosphere at two heating rates 3 and 10°C min^{-1}, using TG. A good linear relationship was found between the temperature of maximum evolution of volatile matter derived from the DTG curve and the characteristic temperatures indicating the beginning, end and maximum value of the fluid stage of coal. Although the experimental values of the parameters derived from thermogravimetric analysis are affected by the heating rate applied and the design of the apparatus. Li *et al.* [20] applied thermal analysis coupled with TG/MS to the pyrolysis of Chinese coals with different ranks. The main evolved pyrolysis products were identified through the on-line recorded mass spectra. The thermal and evolution behavior was compared between the coals. The results showed a strong thermal and evaluation behavior dependence on the coal rank. Different aliphatic fragments and also some aromatic substances, which are of environmental concern, were found to be released depending on the different types of coal. Ozbas *et al.* [21] determined the effect of heating rate on the thermal properties and kinetics of raw and cleaned coal samples by TG/DTG. Experiments were carried out at four different heating rates (5, 10, 15 and 20°C min^{-1}.). Generally, for all of the samples higher peak and burnout temperatures were measured with an increasing heating rate. Kinetic parameters of the samples were determined using an Arrhenius-type kinetic model, and it was observed that activation energies of all the samples were affected inversely when the heating rate was increased. Kızgut and Yılmaz [22] investigated the thermal behavior of five bituminous coal samples in non-isothermal condition by thermal analysis. The integral method was used in the analysis of TG data in order to determine the decomposition kinetics. The main region of the sample's mass loss, arising from the conversion of organic matter to gas, occurred within the temperature range 400–600°C. The thermal parameters derived from TG and DTG curves were correlated with petrographic, proximate and ultimate analyses data. The results indicated that H/C ratio, fuel ratio, mean vitrinite reflectance and petrofactor could be qualitatively used in the prediction of the TG and burning behavior of various rank bituminous coals. Douda *et al.* [23] investigated the structure of an asphaltene sample by TG and DTA in an inert nitrogen atmosphere. The saturated fraction pyrolysis products of the asphaltene consist of paraffins (C-7 to C-20) and cyclo-paraffins (from mono- to hexacyclo-). The coke, asphaltene and maltene groups of compounds have been obtained and analyzed quantitatively. The maltene group of asphaltene pyrolysis products has been separated by high performance liquid chromatography into the saturated, aromatics and polar compounds.The aromatic fraction includes from mono- to penta-aromatic and thiophenearomatic compounds. The polar fraction includes esters, ketons, amides, acids and alcohols. Strezov *et al.* [24] measured the apparent specific heat of coal by employing a computational calorimetric technique during continuous pyrolysis at heating rates of 10, 25 and 100°C min^{-1}. For all of the examined heating rates, the apparent specific heat was found to be approximately 1.4 kJ kg^{-1} K^{-1} at room temperature. When the sample reached decomposition temperature, the specific heat increased to 1.9 kJ kg^{-1} K^{-1}. From this point, the apparent specific heat was greatly influenced by the coal reaction mechanism. For this purpose a detailed gas analysis was carried out for the three examined heating rates. It was found that with increased heating rates, the devolatilisation reactions were shifted to higher temperatures, as reflected in the measured apparent specific heat. Pietrzak and Wachowski [25] studied the high sulphur content coals by TG-DTG. The results have shown that demineralization has no effect on the temperature range of the maximum mass loss. The coal samples have been shown to be characterized by a narrower temperature range of the main devolatilisation peak (380–500°C). The most pronounced structural changes in coal have been found to occur as a result of its oxidation by 5% nitric acid. After such a process of oxidation a new peak of devolatilisation appears with a maximum at 265°C, which can be assigned to the compounds having nitric groups in their structure. Arenillas *et al.* [26] studied the ignition behavior of a series of coal blends, made up from three coals of different rank, sub-bituminous, high volatile and low volatile bituminous, was studied. To this end a thermogravimetric analyzer linked to a mass spectrometer for evolved gas analysis was used. Different ignition behavior was observed for the coals studied; the sub-bituminous and low volatile bituminous coals ignited heterogeneously, while homogeneous ignition occurred for the high volatile bituminous coal. In the case of blends of the low and high volatile bituminous coals, different mechanisms of ignition were observed depending on the blends composition. Kök [27] used DSC and TG/DTG to obtain information on the temperature-controlled combustion characteristics of seventeen coals of different origin. The DSC/TG curves clearly demonstrate distinct transitional stages in the entire coal samples studied. Reaction intervals, peak and bum-out temperatures of the coal samples are also determined. Two different kinetic methods known as, Arrhenius and Coats–Redfern were used to analyze the kinetic data and the results are discussed. Duz *et al.* [28] examined the relationship between particle size and chemical composition of coal sample by elemental analysis and by thermogravimetric pyrolysis with five different particle size ranges. Kinetic parameters of the samples were determined using a Coats and Redfern kinetic model, assuming a first-order reaction. Depending on the particle size of the coal samples, the mean activation energy values varied between 49.1 and 84.6 kJ mol^{-1}. The results discussed indicate that activation energies increase as the particle size decreases. Yu *et al.* [29] studied the effect of particle size on the proximate composition and combustion properties of coal samples by TG, DTG and DSC. When particle size decreased, the content of fixed carbon decreased and that of ash decreased and then increased. Combustion experiments in a thermo balance revealed that with increasing particle size, the whole burning profile shifted to higher temperatures, resulting in an increase in characteristic temperatures. It implied that finer coal particles exhibited higher reactivity. The results also indicated that simultaneous reactions of volatiles and char might happen at low temperatures for small particles. Kök *et al.* [30] performed a laboratory work to observe the combustion characteristics and reaction kinetics of asphaltite. A total of twelve experiments were performed with two different mesh sizes and under three different pressures. Product gas analyses were used to determine atomic H/C ratio, relative reaction rate, activation energy and Arrhenius constant for each asphaltite sample studied. The relative reaction rate *vs.* inverse temperature plots of Silopi asphaltite showed two main reactivity regions. One is occurring in the low temperature region and the other is in the high temperature region. In the low temperature region, an early production was observed where the volatiles within the asphaltite were released; remaining heavy hydrocarbons caused the formation of the second, high temperature region. Lopez-Fonseca *et al.* [31] used non-isothermal thermogravimetric data to evaluate the activation energy and the pre-exponential factor of the combustion of two carbonaceous materials. The research reports on the application of model-free isoconversional methods (Flynn–Wall–Ozawa and Kissinger methods) for evaluating the activation energy of the combustion process. On the other hand, by means of the compensation relation between activation energy and the pre-exponential factor, which was established by the model-dependent Coats–Redfern method, the value of the pre-exponential factor was estimated from the known value of the model-independent activation energy. Gunes and Gunes [32] investigated the kinetic model that describes the mass loss of coals under pyrolysis conditions. Non-isothermal thermogravimetric analysis data on coals have been compared with the predictions of single first-order and distributed activation energy models. It was observed that the distributed activation energy model appears to provide a quantitatively satisfactory description of the devolatilization behavior of coals. Elbeyli and Piskin [33] determined the thermal characteristics and kinetic parameters of lignite sample using thermal analysis system both for combustion and pyrolysis reactions. Non-isothermal heating conditions were applied and reaction intervals were determined for combustion and pyrolysis reactions from obtained curves. The combustion properties were evaluation by considering the burning profile of the lignite sample. Burning temperatures and rate of combustion were determined from TG/DTG curves. Activation energy and pre-exponential factor were calculated from the TG data by using a Coats–Redfern kinetic model both for combustion and pyrolysis reactions. Mianowski *et al.* [34] carried out the combustion of brick-shaped carbonaceous materials in thermo balance in static air. Analysis of kinetics of the process was carried out using both different methods. The results obtained show that, independently on kinetic variables used in differential equations, kinetics of combustion of brick-shaped carbonaceous materials is characterized by only one pair of Arrhenius coefficients: as activation energy and pre-exponential constant. Elbeyli [35] investigated pyrolysis properties and kinetic analysis of asphaltite sample by means of TG. TG/DTG curves showed that the decomposition proceeds through two steps corresponding to the mass loss obtained. Kinetic analysis of the asphaltite decomposition steps was carried out under non-isothermal conditions. Coats–Redfern method was used to analyze the TG data for determination of kinetic parameters. Activation energies and pre-exponential factors were calculated for different heating rates and compared. Biswas *et al.* [36] studied the combustion behavior of two coals of same rank with wide variation in mineral matter content using TG. The burnout temperature and peak temperature showed a linearly decreasing trend with the increasing proportion of the high ash coal. Deviation from the linear trend was observed in the case of the reactivity parameter. The high ash coal showed better TG reactivity than the low ash coal. There was mentioned that the higher TG reactivity could arise from the combined effect of mineral matter and the nature and distribution of the maceral, particularly those of the inertinite group. Kaljuvee *et al.* [37] used coupled TG-FTIR technique for identification of gaseous compounds evolved at thermal treatment of six coal samples from different deposits. The experiments were carried out under dynamic heating conditions up to 900°C at heating rates of 5, 10 or 50 K min^{-1}, in a stream of dry air. The emission of CO_2, H_2O, CO, SO_2, COS, methane, methanol, formic acid, formaldehyde, acetaldehyde, and chlorobenzene was clearly identified in FTIR spectra of the samples studied. Sun *et al.* [38] studied the pyrolysis of coal maceral using TG. The volatile matter evolved in primary and secondary devolatilization and devolatilization kinetics were studied. The volatile matter evolved during primary devolatilization is the major part of the total volatile matter, especially for vitrinite. The percentage of volatile matter evolved during primary and secondary devolatilization suggested that inertinite have higher thermal stability. Though the heating rate can affect the percentage of volatile matter evolved during primary and secondary devolatilization, the order of volatile matter in all the temperature range was the same. Haykırı *et al.* [39] investigated the combustion characteristics of coking, semi-coking, and non-coking Turkish bituminous coal samples applying DTA and DTG techniques. The thermal data from both techniques showed some differences depending on the proximate analyses of the samples. Noncombustible components of the volatile matter led to important changes in thermal behavior. The data from both methods were evaluated jointly and some thermal properties were interpreted considering these methods in a complementary combination. Wachowski and Hoffman [40] studied the effect of ammoxidation on thermal stability of carbonaceous materials characterized by degree of coalification other than that of brown coal or sub-bituminous coal by thermogravimetry (TG-DTG). Analysis of TG-DTG curves has shown that coal samples ammoxidised at the higher temperature show slightly lower thermal stability. It has been established the importance of the sequence in the processes of carbonization and ammoxidation. Both the amount of nitrogen introduced on the surface of studied carbonaceous materials and the thermal stability of nitrogen groups were affected.

Application of thermal analysis techniques on crude oil samples

Much of the work on thermal analysis of crude oils was directed towards the combustion and/or pyrolysis behavior of the samples and kinetic studies. Effect of different metallic additives on the combustion properties of crude oils is also studied. Abu-Khamsin *et al.* [41] investigated the spontaneous ignition potential of a super-light crude oil employing adiabatic, packed-bed reactors. Various process parameters such as initial reactor temperature, oxidant gas flux, oxygen concentration in the oxidant gas, initial oil and water saturations and reactor pressure were varied to determine the set of conditions that would cause the sand-oil mixture to ignite spontaneously. All attempts to ignite the oil failed even when very favorable ignition conditions were tested including 174°C initial temperature, 7340 kPa reactor pressure, 40% oxygen in the oxidant gas and 26 h of oxidation time. Failure of the super-light crude to self-ignite was thought to be due to its low content of unsaturated, mainly aromatics and asphaltene. Al-Saffar *et al.* [42] studied the oxidation behavior of a North Sea light crude oil and its individual SARA fractions (saturates, aromatics, resins and asphaltene) in the presence of consolidated cores. These investigations were made in an attempt to determine the feasibility of air injection into deep light oil reservoirs, and the extent of any interactions between the fractions in a whole oil sample by comparing the behavior of pure fractions with the behavior of mixtures of these fractions in the crude oil. A DISC reactor tan oxidation cell has been used to study the various oxidation reactions and kinetics of a light oil under high pressure and a constant heating rate, by following the concentrations of the gases evolved (CO_2, CO) and consumed (O_2). Such an investigation allows a quantitative study of the temperature intervals at which evaporation, oxidation, and combustion effects operate for each fraction. The data from these experiments may be used to assist the development of a comprehensive simulator for thermal oil recovery. One aim of the overall work is to replace the conventional two pseudo-component representation of crude oil (heavy and light) by a SARA representation with its accompanying interaction and inter-conversion reactions together with the conventional oxidation reactions. This approach should provide a more realistic representation of the oil oxidation process. Goncalves *et al.* [43] reported the application of thermal analysis techniques to study the thermal behavior of asphaltene from Brazilian oil. The approach involves kinetic studies of the thermal decomposition of asphaltene under controlled conditions by TG, characterization of volatile fractions by TG and DTA coupled with TG-DTA/GC/MS and by GC/MS in the volatile recovered. The coke formed was also studied after being decomposed into smaller molecules using selective oxidation. Alaoui *et al.* [44] the conservation of argon oil by TG. The argon oil, to edible or cosmetic use and owing to its wealth in essential fatty acids (linoleic acid (33.15%) and oleic acid (46.65%)), is able to reduce the rate of blood cholesterol and to warning the atherosclerosis. This work is a contribution to the determination of the characteristics of this particular oil. The studies showed that the oil preserves relatively well by resisting several months to the oxygen owing to the presence of polyphenols and tocopherols. It becomes degradable easily when it is carried to 64°C for several days. Kök [45] applied simultaneous TG-DTA to characterize the light crude oil combustion in the presence and absence of metal oxide. In crude oil-limestone mixture, three main transitional stages are detected. These are distillation, low-temperature oxidation (LTO) and high temperature oxidation (HTO) regions respectively. In the case of experiments with Fe-chloride at different amounts, the shape of TG-DTA curve is changed considerably. Kinetic parameters of the samples are determined using ASTM method. Reduction in activation energy is considered to be an indication of the catalytic activity of the additive. Kök [46] investigated the reaction rates related to an in-situ combustion process and the effect of heating rate and crude oil type on the reaction rates. A laboratory model was used to run reaction kinetic experiments in unconsolidated limestone packs using three different crude oils. Experiments were performed under the same pressure and airflow rate and at two different heating rates. It was observed that oxidation of crude oil porous media follows a series of reactions. These reactions can be divided into three regions: low temperature oxidation, fuel deposition, and high temperature oxidation. Produced gas analysis was used to determine the activation energy of the samples. Experiments were also performed with TG/DTG, and the results are discussed. Sonibare *et al.* [47] studied the thermal behavior of the Nigerian oil sand bitumen in an oxidizing environment using non-isothermal TG and DTA. Three regions of mass loss corresponding to low-temperature oxidation, fuel deposition and high temperature oxidation were identified. Increasing the heating rate caused a shift in the reaction regions and peak temperatures to higher temperatures. No effect of gas flow rate was observed on the reactions. The oil sands have lower peak temperatures and activation energies compared with their corresponding bitumen extracts, suggesting a catalytic effect of sand on the reactions. The DTA revealed the exothermic nature of the reactions. The exothermicity increased with increasing heating rate. The results of this study showed that the heating rate and the presence of sand have significant effect on the thermo-oxidative reactions of the bitumen. Kök and Bagci [48] studied the light crude oil combustion and kinetics in the presence of copper chloride and magnesium chloride by TG-DTA. In TG-DTA experiments with magnesium chloride, three reaction regions were identified, known as distillation, LTO and HTO. In the case of copper chloride, two main transitional stages are observed with distillation and HTO. It was also observed that, as the mol% of magnesium chloride increased, the high-temperature oxidation peak shifted to the lower-temperature region reflecting more homogeneous composition of the solid residue. In the case of reaction cell experiments, it was observed that the molar CO_2/CO ratio values of fuel combustion increased with the addition of metallic salts. A decrease in the atomic H/C ratio with an increase in temperature was observed in all experiments performed. Li *et al.* [49] used TG-DTA techniques to investigate oxidation behavior using thermal fingerprinting effects on pure paraffin samples and mixtures of pure components with crude oil. The results demonstrated that each paraffin sample shows different oxidation behaviors at low temperatures and high temperatures. The fractions lighter than C16 distill before they reach a temperature where oxidation reactions are significant. Only low temperature exothermic activities are apparent for the fractions between C16 and C26. The heavier fractions show both low and high temperature exothermic activities. The lower molecular mass samples show lower onset temperatures for oxidation reactions. With increasing molecular mass, the exothermic peak temperatures both in the low and high temperature regions shift to higher temperatures and increased energy release. Kök *et al.* [50] determined the combustion characteristics of crude oils in the presence of a limestone matrix using TG/DTG. In combustion with air, three distinct reaction regions were identified in all crude oil/limestone mixtures studied known as LTO, fuel deposition (FD) and HTO. The individual activation energies for each reaction region may be attributed to different reaction mechanisms, but they do not give any indication of the contribution of each region to the overall reactivity of the crude oils. Depending on the characteristics, the mean activation energy of samples varied between 50.3 and 55.8 kJ mol^{-1}. Goncalves *et al.* [51] applied TG to evaluate the thermal behavior of five refinery atmospheric distillation residues (ATR) obtained from different Brazilian crude oils. The asphaltene were extracted of each sample and their influence on coke formation was studied. It was observed that they have a great contribution on carbonaceous residues formation during pyrolysis and that the heavier the ATR sample, the higher is the contribution of other heavy components present in ATR samples. Batina *et al.* [52] prepared thin films of crude oil samples for atomic force microscopy (AFM) analysis on the gold substrate. Sample preparation involved evaporation during a long (24 h) but mild thermal exposure (80°C). FTIR microscopy (reflectance spectroscopy) was employed to determinate the quality of the thin film surface, before the morphology characterization. The surface reflectance spectra were compared to direct transmittance FTIR of liquid oil samples. The two FTIR techniques showed different spectral characteristics related to oxygenated functionalities. This clearly indicated that the surface of the thin films of the oil samples prepared for AFM is oxidized. Oil samples of different origin show different degrees of oxidation seen by the development of carboxylic acid vibrations at 1750 cm^{-1} as well as vibrations in the 1300–1100 cm^{-1} region. The relative degree of oxidation state was compared to surface morphology data by AFM previously reported. The reported results emphasize the advantage of complementary techniques (AFM/FTIR microscopy) in the analysis of petroleum thin films that should be considered during analysis and interpretation of this type of data. Dong *et al.* [53] used thermogravimetry to determine the pyrolysis kinetics of the asphaltene of Chinese crude oil. The distributed activation energy model (DAEM) was used to analyze these complex systems. The results show that the peak activation energy for pyrolysis of the asphaltene is 245 kJ mol^{-1} and the pre-exponential factor is $5.88\cdot10^{14}$ s^{-1}. A linear relationship can be found from the plots of logarithm of the pre-exponential factor against the activation energy at selected conversion values. This phenomenon known as the compensation effect was explained and it was in agreement with the estimated chemical structure determined by NMR. Freitag and Verkoczy [54] studied the LTO reactions of the SARA fractions separated from two crude oils in the presence of their reservoir sands at temperatures between 130 and 230°C. The results indicated that the usual approach to modeling LTO – the use of a very few single-step Arrhenius-rate equations – could not be made to reflect the observed reaction kinetics. Instead, this investigation found that the following reaction characteristics were needed for accurate reaction modeling: a change in the order of reaction with respect to oxygen concentration from 1/2 to 1 as temperature rises; the repression of a saturates oxidation reaction by other fractions; and, a prominent induction period exhibited by the saturates fraction. The compositions and yields of the ultimate LTO reaction products were measured, and these included relatively stable residues with high oxygen contents. Because the LTO reactions play an important role in enhanced oil recovery by air injection methods, the above information is valuable for the simulation and prediction of these processes. Kök [55] investigated the role of clay on the combustion and kinetic behavior of crude oils in limestone matrix. For this purpose, simultaneous TG-DTA experiments were performed at three different heating rates as 10–15 and 20°C min^{-1}, respectively. A uniform trend of decreasing activation energies was observed with the addition of clay. It was concluded that clays surface area affects the values of Arrhenius constant, while it is the catalytic properties of clay, which lower the activation energies of all the reactions, involved in the combustion process. Ambalae *et al.* [56] used TG to obtain information on the pyrolysis and combustion behavior of both crude oil and its asphaltene, each mixed with reservoir sand. Of all the saturate, aromatic, resin, and asphaltene fractions, asphaltene contribute the most to the formation of coke (fuel). Temperature-ramped as well as the isothermal pyrolysis experiments on whole oil and asphaltene were analyzed to determine the temperature at which coke formation was maximized. Furthermore, isothermal combustion curves for coke derived from whole oil and asphaltene were obtained to provide reliable data for calculating the kinetics of the reactions. The classical Arrhenius model was applied, and the activation energy for the combustion of coke formed from pure asphaltene and from the whole oil was calculated. The results showed that the Arrhenius model fitted the data well in the entire range of temperatures the experiments were conducted. The source material for the coke led to modest differences in its reactivity. The observed activation energy for asphaltene was 117.7 kJ mol^{-1}, and for the whole oil it was 129.5 kJ mol^{-1}, which indicates that they were in close agreement. Also, the combustion of coke from asphaltene showed a reaction order of 0.4 at 375°C, which gradually increased to 0.9 at 525°C. For whole oil, it increased from 0.5 at 375°C to 0.7 at 500°C. Shiskin [57] used high-resolution DSC to accurately establish the temperature intervals of oxidation/distillation of the major components of crude oils. The experimental TG-DSC curves show that the temperature scan of the run can be divided into six regions, of which the first belongs to simple distillation of the sample's liquid constituent (the distillate) and the others to oxidative cracking distillation of the solid (heavy) residue. The latter occur in the order paraffins+light oils, middle base oils, heavy base oils, condensed aromatics (resins) and asphaltene. The probable oxidation mechanisms of different classes of petroleum hydrocarbons operating in different temperature regions are discussed. Full quantitative fractional and group component analysis of a number of crude oils of different chemical classes and geological age was carried out by the combined TG-DSC techniques under specially chosen experimental conditions. Kök and Acar [58] investigated the thermal characterization and kinetics of light crude oil in the presence of limestone matrix. TG/DTG is used to characterize the crude oil in the temperature range of

20–900°C, at 10°C $\min^{-1}$ heating rate using air flow rate of 20 mL $\min^{-1}$. In combustion with air, three distinct reaction regions were identified known as LTO, FD and HTO. Five different kinetic methods used to analyze the TG/DTG data to identify reaction parameters as activation energy and Arrhenius constant. On the other hand different $f(\alpha)$ models from literature were also applied to make comparison. It was observed that HTO activation energy of light crude oil is varied between 54.1 and 86.1 kJ mol^{-1} while LTO is varied between 6.9 and 8.9 kJ mol^{-1}. Shiskin [59] used a calorimetric-thermogravimetric method of determining mass% contents of distillate fractions, paraffins, base oils, resins, asphaltene and carbines in various crude oils. The method is based on recording DSC curves of a 10–15 mg sample heated in air in a calorimetric-cell at a rate of 40–50°C $\min^{-1}$. Additionally, mass loss of sample is found at temperatures before and after the reaction. At temperatures from 220°C or higher distillation of the hydrocarbon mixture starts to be accompanied by its exothermic oxidation, thereby making possible monitoring the distillation (oxidation) of consecutive HC fractions by simple calorimetric-techniques. Differential scanning calorimeter 'Thermodat' of high-calorimetric-resolution and sensitivity equipped with dedicated software was used for conducting the experiments and performing all the calculations. Percent contents of the main constituents in a number of heavy and light crude oils were determined and formulas for establishing paraffinic, base oil and coke-forming potentials of crude oils and oil residues derived. One full analysis of a sample takes no longer than 1.0–1.5 h. The method can be used for on-line quality control of various petroleum products, such as atmospheric and vacuum oil residues. cracking residues, lubricants, ceresins and paraffins. Li *et al.* [60] examined the oxidation, behavior of three crude oils (a light oil, a medium oil and an Athabasca bitumen) by using the pressurized differential scanning calorimeter (PDSC) at pressures from 110 to 6.894 kPa. Pure hydrocarbon aromatics and paraffin samples were also selected for the current study. The study shows an increase of pressure results in an increase in the rate of oxidation reactions and heat released from the oxidation reactions. The PDSC heat flow curves also clearly demonstrate the effect of chemical structure of the samples on their oxidation behavior. The extent of oxidation of hydrocarbon samples is strongly dependent on the nature of the hydrocarbon. Goncalves *et al.* [61] applied thermogravimetry to evaluate the heavy distillation residues of different Brazilian crude oils. The thermal characteristic of the samples could be studied by only one experiment. It was possible to evidence the linear correlations among the results obtained by the TG curves and by the patterned methodologies, therefore anticipating volatile and carbonaceous materials (coke) formed during their thermal cracking. The correlations herewith observed, in a short period of time, provided comparisons among the petroleum fractions. Falla *et al.* [62] proposed a methodology for the estimation of the SimDis (Simulated Distillation) properties of crude petroleum based on NIR (Near Infrared) spectroscopy. In the proposed methodology, a NIR transmission probe is used and no desalting or thermal conditioning is applied to the samples before measurement. In order to build the correlations, forty petroleum samples with API grades ranging from 31.1 to 36.4 were employed. The NIR spectral data were correlated with the SimDis curves (mass% vaporized at a given temperature) and the salt content of the petroleum by neural network techniques. The resulting network reproduced quite accurately the SimDis curves, showing the technical feasibility of the proposed methodology.

Application of thermal analysis techniques on oil shale samples

Much of the work on thermal analysis of oil shale samples was directed towards characterization, pyrolysis and combustion behavior and kinetic analysis. Jaber and Mohsen [63] investigated the drying kinetics of two oil shales from different deposits over a temperature range of 70–150°C in TG/DTG 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. Kök [64] presented the results of experimental study on the thermal investigation of Seyitömer oil shale sample. TG/DTG and DSC were used to determine the thermal behavior of the oil shale sample. From the experiments and kinetic analysis, it was observed that Seyitömer oil shale sample have more than one reaction region where the activation energies of the first region are higher. Higher heating rates resulted in higher reaction temperatures both in DSC and TG/DTG experiments. Torrento and Galan [65] studied the kinetics of the thermal decomposition of Spanish oil shale using isothermal and non-isothermal TG. The non-isothermal mass-loss data was analyzed at different heating rates (5, 10, 15, 20 and 50 K $\min^{-1}$) up to 1173 K and for a particle size of $0.250\cdot10^{-3}$ m. Three methods were applied for the determination of the kinetic parameters: the direct Arrhenius plot method, the integral method and the differential method. The results obtained from the isothermal method give an apparent activation energy of 150 kJ mol^{-1} and a frequency factor of $2.11 \cdot 10^8$ s^{-1}, while for the non-isothermal method these results were 167 kJ mol^{-1} for activation energy and $2.16 \cdot 10^9$ s^{-1} for frequency factor. Kök *et al.* [66] studied the thermal and organic geochemical investigation of oil shale sample. TG/DTG and DSC have been used to determine the thermal behavior of the oil shale sample. On the other hand, organic carbon content, rock-eval pyrolysis, and gas and liquid chromatography experiments were conducted to determine geochemical properties of the oil shale sample. Kök [67] studied the thermal characteristics of three Turkish oil shales (Himmetoğlu, Beypazarı and Hatıldağ) by thermal analysis techniques (DSC, TG and PDSC). Two distinct exothermic peaks were identified in all experiments known as low-temperature oxidation and high-temperature oxidation reaction regions. Kinetic data were analyzed by Arrhenius, and Coats and Redfern models and the results are discussed. Ballıca and Larsen [68] investigated the effect of temperature and heating rate on the cross-link density of char samples obtained by pyrolysing Göynük oil shale using the volumetric solvent swelling technique. The cross-link density decreases slightly with increasing pyrolysis temperature. The heating rate and thus the pyrolysis time had at most a small effect on the cross-link density. Char-solvent interactions do not follow regular solution theory. The demineralized kerogen swells more than does the native kerogen (16% ash). Kök and Pamir [69] studied the kinetics of oil shale pyrolysis by DSC and non-isothermal TG. In nitrogen atmosphere two different mechanisms causing mass loss were observed: distillation in the region between ambient temperature and 500 K, visbreaking and cracking in the region of 500–800 K. Kinetic parameters of the sample pyrolysis are determined using different kinetic models, and the results are discussed. Karayıldırım *et al.* [70] investigated the effect of mineral matrix on thermal degradation of Göynük oil shale and Şırnak asphaltite, in a thermogravimetric analyzer. Initial and HCl-washed samples showed similar degradation behavior, while HNO_3 washing affected it in both cases. Changes in organic structure, which is different for shale and asphaltite the former being aliphatic, and the latter having aromatic character after HNO_3 treatment affected the degradation kinetics of the samples differently.

Kaljuvee *et al.* [71] used the combined TG-FTIR techniques for studying the gaseous compounds evolved at thermo-oxidation of oil shale samples from different deposits (Estonia, Jordan, Israel). In addition to H_2O and CO_2 as the major species, the formation and emission of CO, SO_2, HCl and a number of organic species as methane, ethane, ethylene, methanol, formic acid, formaldehyde, chlorobenzene, etc. was determined. Differences in the absorbance of respective bands in FTIR spectra depending on the origin of oil shale and on the heating rate used were established. Barkia *et al.* [72] used thermal analysis to determine the impact of heating on the decomposition reaction of two Moroccan oil shales between ambient temperature and 500°C. During pyrolysis of raw oil shale, the residual organic matter (residual carbon) obtained for both shales depends on the heating rate (5 to 40°C min^{-1}). Three stages characterize the overall process: the concentration of carbonaceous residue decreases with increase of heating rate, become stable around 12°C min^{-1} and continue to decrease at higher heating rates. Activation energies were determined using the Coats–Redfern method. Results show a change in the reaction mechanism at around 350°C. Below this temperature, the activation energy was 41.3 kJ mol^{-1} for the decomposition of Timahdit, and 40.5 kJ mol^{-1} for Tarfaya shale. Above this temperature the respective values are 64.3 and 61.3 kJ mol^{-1}. Sonibare *et al.* [73] studied the thermal decomposition of Lokpanta oil shale from Nigeria by non-isothermal TG and DTA. The geochemical characteristics of the oil shale were also investigated by Rock Eval. pyrolysis. Thermal breakdown of the kerogen content of the oil shale takes place mainly at the temperature range of 300 to 570°C. The estimated decomposable kerogen content of the oil shale ranges from 4.55 to 9.64 mass%. The activation energies of the pyrolysis process vary from 73.2 to 75.0 kJ mol^{-1}. The DTA data reveals the exothermic nature of the decomposition process. The results from the geochemical analysis indicate that the oil shale contains sufficient, good quality kerogen to generate both oil and gas upon pyrolysis.

Bhargaya *et al.* [74] used TG, diffuse reflectance infrared Fourier transforms spectroscopy (DRIFTS) and X-ray diffraction (XRD) in conjunction to characterize oil shale samples from an Australian Tertiary oil shale deposit. It was evident from TG analysis that the mass loss in the 450–550°C temperature region has a strong and direct correlation with the amount of oil in the samples, as determined by the MFA method. Calibration curves were generated in which oil content can be predicted from TG and DRIFTS data. The combination of TG and DRIFTS is mostly useful in examining organic matter in oil shale while DRIFTS and XRD combination is useful in examining the minerals phases. Combination of these three techniques can provide an alternative and inexpensive method to the MFA analysis in determining the kerogen content, while overcoming the limitations of each other. Abu-Quadis *et al.* [75] studied the oil shale samples from different seem of the Attarat deposit in Jordan using a thermogravimetric analyzer. The influence of grain size and heating rate (from 3 to 40°C min^{-1}) on the process of thermal degradation of the shale sample has been determined. The integral method was used to analyze TG data in order to determine pyrolysis kinetics. The main mass loss of the samples, arising from the conversion of organic matter to oil and gas, occurred within the temperature range from 250 to 550°C. The magnitude of the total mass loss was mainly dependent on the furnace temperature and, to a lesser extent, on the heating rate employed. The decomposition rate of the studied samples changed significantly at a critical temperature of about 300±10°C. The kinetic results obtained are in agreement with those reported, for other Jordanian oil shales from different deposits. Değirmenci and Durusoy [76] investigated the pyrolysis kinetics of –210+149, –250+210 and –420+250 mm particle size Göynük oil shale under non-isothermal conditions with a heating rate of 10–60 K min^{-1} in the 298–1173 K pyrolysis temperature interval under argon atmosphere. The pyrolysis characteristics of the samples were analyzed using TG/DTG curves. DTG data were analyzed by a model assuming first order kinetics. Minimum activation energy was obtained as 0.6 kJ mol^{-1} with 60 K min^{-1} in –210+149 mm. It appears from the results that higher heating rate values have a limiting effect on the behavior of the pyrolysis reaction. Jiang *et al.* [77] conducted co-combustion experiments of mixture of Huadian oil shale and Heshan coal with high sulphur content using a thermogravimetric analyzer. The effects of five different Ca/S mol ratios on the combustion characteristics of mixture fuel are analyzed using TG and DTG curves. The results show that the initial temperature of combustion of mixture fuel is decreased with an increase in the oil shale content of mixture fuel. The combustion characteristic of mixture fuel is superior to that of Heshan coal. Adding about 20 mass% Huadian oil shale into Heshan coal is feasible for desulphurization of mixture fuel during combustion. Han *et al.* [78] conducted combustion and pyrolysis experiments of Huadian oil shale using a thermogravimetric analyzer. The effect of various factors on combustion of oil shale is studied. Particle size has little effect on combustion process of oil shale; starting temperature of combustion mass loss and ignition temperature of oil shale decrease with increasing O_2 concentration of ambient gas; increase of heating rate can result in ignition temperature, burn-out temperature and maximum rate of combustion mass loss increasing. Homogeneous ignition mechanism of oil shale is ascertained using a hot state microscope. Activation energy was determined using Arrhenius model that is solved by Freeman–Carroll method. Calculation results show activation energy will increase with heating rate.

Conclusions

This review reveals that thermal analysis techniques are finding an increasing application in the study of fossil fuel characterization. Use of these techniques has considerable significance in terms of the determination of the changes in properties including pyrolysis and combustion phenomena, particle size and heating rate effects, calorific value effects and kinetics. The review showed that thermal methods were important not only theoretically but also from a practical point of view.

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