

Review

APPLICATION OF THERMAL ANALYSIS FOR INVESTIGATING LIQUID FUELS, PETROLEUM- AND COKE-CHEMICAL PRODUCTS

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Liquid fuels are hydrocarbon fractions (gasoline, diesel, solar, etc.) obtained by the distillation of oil or of different tars resulting from the thermochemical processing (coking, pyrolysis, gasification, etc.) of solid fuels. Some may be individual chemical compounds (benzene, toluene, ethanol, etc.), while others are mixtures of thousands of compounds of high molecular weight (asphalts, bitumens, pitches, etc.), which are solid at ordinary temperatures. The numerous mineral lubricating oils (mixtures of different groups of hydrocarbons, i.e. paraffinic, naphthenic and aromatic hydrocarbons) belong here, as well as the lubricants which are colloid systems of hydrocarbons and metal soaps. These products also comprise synthetic and natural waxes, consisting predominantly of hydrocarbons or esters.

Thermal analysis is being used increasingly frequently for studying the above products, which are of exceptional significance for industry and for the economy. Using micro-DTA equipment, experiments have been carried out to determine the boiling points of hydrocarbons [1–4]. Lewis and Edstrom [5], who have studied the behaviour of different polynuclear aromatic hydrocarbons when heated in a thermal analysis apparatus, have found that the stable and non-reactive compounds (e.g. naphthalene and perylene), which evaporate totally without being decomposed, show two endothermic effects in the DTA curve, characterizing their melting and boiling points. With thermally unstable and reactive aromatic hydrocarbons (acenaphthylene, tetracene, etc.) which decompose partially or totally even before reaching the boiling point, there is only occasionally a weak endothermic effect, which is due to their evaporation. The frequently observed exothermic effects in the above-mentioned aromatic hydrocarbons are due to polymerization and polycondensation processes.

On performing thermal analysis of *n*-docosene and naphthalene, Rustschev [6] has found characteristic endothermic effects, with maxima at 42°C and 80°C respectively, which coincide with the melting temperatures of these compounds. Broad endothermic peaks at 110°C and 113°C respectively,

were also found for dimethylnaphthalene and fluorene, resulting from a transition from the solid to the liquid state. The sublimation of naphthalene and dimethylnaphthalene is connected with a clearly manifested endothermic effect at 185°C and 220°C respectively. On the DTA curves for carnauba wax and paraffin there are also endothermic effects at 80°C and 43°C respectively, coinciding with the melting intervals of these products. The TG curve for paraffin is characterized by several clearly manifested steps in the 400–500 K temperature region, which are due to the successive evaporation of hydrocarbons with an increasing number of carbon atoms [6,7]. Thermal analysis of normal paraffin hydrocarbons has shown a correlation between the boiling points of 10% and 25% of their mass, the maximum found in the hydrocarbons studied [8].

Joncich and Bailey [9], who are conducting thermal analyses and studying the diagrams reflecting the melting of binary systems of anthracene and phenanthrene, have not observed complete fusion in the solid and liquid state, and they claim that these are peri-eutectic transformations. Handley [10] subjected the DTA curves for benzene to quantitative evaluation and succeeded in determining the percentage of polluting admixtures (0.01% to 0.65%), applying Herington's theory [11]. This was later expanded by Friedenberg and Jahnke [12], who succeeded in demonstrating 0.0008% admixtures in naphthalene using the DTA curve.

Adnoyi [13–15] has conducted original research on the evaporation and thermal decomposition of different mineral oils and their mixtures with benzene and cyclohexane. Later, Adonyi and Körösi [16,17] used thermal analysis to study the kinetics of evaporation of hydrocarbon mixtures containing benzene, toluene, cyclohexane and *n*-heptane. Adonyi et al. [18–20] are presently applying successfully thermogravimetric analysis for quantitative characterization of motor oils. Vamos et al. [21] have also used thermal analysis successfully for studying the thermal stability and tribological properties of additives to oils containing chlorine and sulphur.

Wieckowska [22] has performed thermal analysis on six samples of heavy oil residues, and has found that their thermal decomposition starts above 400°C and is fastest in the region 460–470°C. Up to 520°C about 75–80% of the organic mass of these oil residues is transformed into volatile products. Csikos et al. [23] have used thermal analysis for characterizing various resins obtained from the oil remaining as a waste product of the pyrolytic production of ethylene. Table 1 presents the results obtained by these authors in their thermogravimetric experiments, showing the existence of a directly proportional relationship between the melting temperature of the resins and the coke residue below 1000°C. In the thermal analysis of different individual hydrocarbons, Rustschev [24] has found a correlation between the melting and boiling temperatures, on the one hand, and between the coking value and the time needed for the formation of 1% coke, on the other (Table 2).

TABLE 1

Thermogravimetric analysis of heavy hydrocarbon resins [23]

Melting temperature (°C)	25	57	90	97	131
DTG peaks (°C)	380	365	380	380	380
	460	460	475	480	460
	610				
DTA peaks (°C)	endothermic				
	80		60	80	130
	380	340	120	380	385
	420		380		440
	490	470	490	430	490
	560				585
	exothermic				
	460	450		420	430
	520	495	520	520	480
	600				
Initial temperature of mass reduction (°C)	90	190	200	240	265
Mass loss (%)					
20–250°C	6.5	2.0	1.5	0.0	0.0
250–300°C	7.5	8.0	3.5	3.0	1.0
300–350°C	16.0	13.0	10.5	9.5	8.5
350–400°C	25.0	27.0	25.5	26.0	23.5
400–450°C	9.0	11.0	13.0	13.0	14.5
450–500°C	6.5	5.0	7.5	9.0	9.5
500–1000°C	11.5	7.0	7.0	8.0	7.0
residue	18.0	26.8	31.0	31.5	36.0

TABLE 2

Physical constants and coking capacity of hydrocarbons [24]

Compound	Temperature (°C)		Coking value (%)	Time for the formation of 1% coke (min)
	Melting	Boiling		
<i>n</i> -Docosane	44.9	380	0.09	1177
Naphthalene	80.0	216	0.11	963
2,6-Dimethyl-naphthalene	111.0	262	0.03	3419
Fluorene	116.0	299	0.19	552
Difluorenyl	249.0	500	17.48	6
Pyrene	150.0	394	3.90	27.2
Chrysene	255.0	441	4.02	26.3
Truxene	369.0	550	71.06	1.5
Brazan	205.0	395	2.06	51.5

Thermal analysis is used successfully for characterizing thermal and oxidative stability [25,26], evaporation [27], and coking of different oil fractions and groups of hydrocarbons [28], as well as for other purposes [29–32]. Penchev and Stoyanova [33] have succeeded in linking the results of the thermal analysis with the chemical composition of high-boiling oil products.

Wieckowska and Bogdanov [34] have performed thermal analysis on residues from the vacuum distillation of oil from Romashkinskoe, and Hernandez and Choren [35], as well as Speight and Pancirov [36] have used this method for determining the thermal stability of oil asphaltenes. Al-Sammerrai [37] has also applied thermal analysis for studying the stability of paraffin and hydrocarbon waxes, and Faust [38] has performed thermal analysis on petrolatum and oil waxes. Vassay et al. [39] have studied the mechanism of oxidation of oil products using a scanning calorimeter, while Ayala et al. [40] are presently using this to study the processes of oxidation of oil products. Adiga et al. [41] have performed thermal analysis on mixtures of oil fractions and alcohols, while Al-Sammerrai [42] applies this method for studying mineral and synthetic oils. Lin et al. [43] have used thermal analysis to study dispersed organic matter, which is of great significance in petroleum geology.

Glushchenko [44] gives the DTA curves for mixtures of different black coals and anthracite with 5% to 20% oil mazout. When 5% mazout is added to the dry coals, an endothermic effect appears in the DTA curve with a maximum at 420 °C, which characterizes the presence of a plastic state, the so-called mersophase. When the quantity of mazout reaches 20%, the DTA curve becomes identical with that of coking coals. Even the thermally stable anthracite becomes reactive when 20% mazout is added to it, and considerable endo- and exothermic effects appear in its DTA curve. The addition of 30% coal pitch to dry coal radically changes the character of the DTA curve.

In many countries in recent years programmes for obtaining stable coal–oil dispersion systems have been worked out with the aim of replacing expensive and deficient liquid fuels. Lin Hao [45,46] was the first to subject similar coal–oil mixtures containing 50% to 75% liquid petroleum products to thermal analysis. Later this researcher, together with Dezhough [47], used DTA curves to study the inflammation of such disperse systems and found an increase in the time needed for burning with increases in the amount of the solid phase. Rustschev and Atanassov [48] have published the DTA and TG curves for various petroleum products (ordinary and cracking mazout, boiler fuel, liquid paraffin, oil extracts, etc.) used as a liquid phase for obtaining fuel disperse systems. These researchers [49] have subjected coal–oil mixtures containing 50–80% mazout and 50–20% coal to thermal analysis, and have found that the activation energy of the liquid suspensions studied (78–109 kJ mol⁻¹) depended on the coal used as the solid phase. Rustschev et al. [50] have applied thermal analysis to the study of these

TABLE 3
Thermal analysis of soaps [60]

Type of soap	Phase transitions (°C)
Li-stearate	117, 200, 225, 229
Co-stearate	99, 108
K-laurate	58, 129, 227, 273
K-myristate	65, 131, 138, 209, 268
K-palmytate	50, 62, 125, 153, 183, 248, 276
K-stearate	66, 128, 170, 178, 193, 268, 350
Al-caprylate	216
Al-caprate	196
Al-laurate	86, 149, 185
Al-myristate	92, 136, 179
Al-palmytate	90, 128, 170
Al-stearate	99, 119, 162
Na-laurate	98, 130, 187, 220, 324
Na-myristate	80, 106, 133, 215, 233, 297
Na-palmytate	114, 135, 209, 237, 292
Na-stearate	89, 114, 134, 208, 238, 280
Ca-stearate	65, 86, 123, 150, 195, 350

mixtures in an oxygen atmosphere, in order to determine the character of their burning and their thermal stability. Rustschev et al. [51] have conducted thermal analysis of fuel disperse systems containing 40% liquid paraffin or mazout and 60% carbon concentrate, obtained by flotation of cinder-ash mixtures from thermoelectric power plants. Rustschev et al. [52] are presently applying this analysis successfully to determine the thermal stability of different carbon-containing aqueous disperse systems used as anti-burning products in casting.

The metal salts of fatty acids (soaps), some of which are used as components in greases and consistent lubricants, have long been subjected to thermal analysis [53–59]. A survey of the data in the literature on phase transitions in the thermal analysis of different soaps, compiled by Trzebowski [60], is given in Table 3. Roth et al. [61] have studied the thermal properties of the ammonium salts of ten different fatty acids, and have found that their decomposition is accompanied by an exothermic effect with a maximum varying from 146°C (ammonium propionate) to 315°C (ammonium stearate). These researchers have found a relationship between the melting temperature of the fatty acids and the nature of the salts, on the one hand, and the length of the hydrocarbon chain on the other. Lorant [62] has performed thermal analysis of the soaps of bivalent metals, and Mehrotra and Rai [63] have used thermogravimetric methods to study thorium and lanthanide soaps of lauric, palmitic, stearic, and behonic acid.

The thermal properties of the soaps and, especially, of the alkali and

alkaline-earth soaps are of great importance for the operational behaviour of the consistent lubricants which are mixtures of these soaps and hydrocarbon oils. These are colloid systems (bi- or multiphase mixtures of oils and soaps), which are stable only in a strictly defined temperature region which can be determined by means of DTA and the soap-hydrocarbon phase diagram. Such model systems of lithium and sodium stearate, aluminium palmitate, myristate, laurate, caprate and caprylate in *n*-hexadecane and Nujol have long been studied [64–69]. Rabl et al. [70] presently apply DTA to lubricants intended to be applied under conditions of high pressure, while Krawetz and Tovrog [71] apply this method to the study of high-melting lubricants.

Slavkov [72] has published the DTA and TG curves for different colloid-graphite mixtures which are widely used in the glass-making industry. Novacheva-Rouneva [73] has studied the influence of prolonged isothermal crystallization on the parameters of lithium lubricants, while Stanoulov [74] has analysed the DTA curves of different calcium-complex lubricants.

Thermal analysis also is applied increasingly for studying pitches obtained during the distilling or modification of various tars. Buttler [75] has studied the influence of heating rate on the thermal destruction of electrode pitch. Soviet researchers [76–78] have also studied the DTA curves for coal pitch for characterization purposes. Rustschev and Atanassova [79] compare the DTA and TG curves of coal pitches with different softening temperatures. New works have appeared recently, whose authors [80–82] are using thermal analysis to study coal pitches. Of particular interest are the experiments of Charply [83] in studying the mechanism of polycondensation in the oxidation of pitch. According to Rustschev [84,85], the DTA and TG curves of the coal pitch are summated, i.e. they are obtained by the superposition of the thousands of curves of the compounds making up this extremely complex product. Schultze [86] also draws attention to the difficulties in interpreting the DTA and TG curves for pitches, bitumens and waxes, which substances are multicomponent mixtures of different organic compounds having similar physico-chemical properties. Lange et al. [87,88] believe that with such products only the end of the melting process can be determined with the help of DTA curves.

Currel and Robinson [89] believe that the determination of individual components by means of thermal analysis is possible only in some special cases, e.g. admixtures to polyethylene. Rustschev et al. [90–92] have determined very accurately the melting temperature of indene-cumaric resins using the characteristic endothermic effect on the DTA curves. This method can be used to study the melting interval, i.e. the transition from the solid to the liquid phase in carnauba wax and petroleum paraffinic hydrocarbons [84,92].

Rustschev et al. [93] have applied thermal analysis to the study of different mixtures of oil and coke-chemical hydrocarbons with poly(vinyl chloride), and have found that petroleum bitumens improve the thermal

stability of these compositions. Charit et al. [94] carry out thermogravimetric analysis of coal pitch and its fractions while Furimsky [95] has studied different pitches and bitumens using thermal analysis. This has been used successfully by Collet and Rand [96], as well as by Barr and Lewis [97], who have also studied coal pitches. Illes [98] applies thermal analysis to kinetic studies on the thermal destruction of hydrocarbons having different molecular masses and chemical structures. Dyszel and Pettitt [99] apply thermal analysis for characterizing carbon waxes, and Gonzalez et al. [100] have found four endothermic transformations on the DTA curves for similar waxes.

Attempts to use thermal analysis for studying bitumens extracted from solid fuels by means of different organic solvents began in the 1950s. The first results show that the DTA curves of the starting coals, the pyridine extract and the residual coal are very similar [44]. De Ruiter [101] has published the DTA curves for bitumens extracted from vitrinite using pyridine or benzene. Rustschev et al. [102–106] have found that the separation of the bitumens from lignite and brown coal results in a reduced exothermic effect at 400°C. Later Rustschev and Atanassov [107] proved that the extraction of bitumens from peat using alcohol–benzene is the reason for the disappearance of the exothermic effect having a maximum at 375°C, though the exothermic effect at 290°C, typical of peat, remains. These researchers give the DTA curve for the peat bitumens, which are characterized by several exo- and endothermic effects in the temperature range 380–450°C. Minkowa et al. [108] divide the peat bitumen into resins and waxes, and subject them to thermal analysis. Zhukov et al. [109] and later Zubko et al. [110] have also used thermal analysis to study bitumens extracted from peat and brown coal and their components (resins, hydrocarbons, etc.). Malovska et al. [111] give the DTA and TG curves for bitumen obtained by extraction from black coal and for its oily and solid components (soluble or insoluble in petroleum ether), differing substantially in the type and intensity of the thermal effects.

The discrepancy between oil reserves and the enormous consumption of liquid fuels has led to the elaboration of different processes for coal liquefaction [112]. Boncheva [113] gives the DTA curve for humic-sapropelitic coal from the Chernomore mine, and discusses changes occurring under the effect of hydrogen when this coal is transformed into liquid products. Mraw et al. [114] apply DCS to the study of synthetic liquid fuels obtained from coal, while Galya et al. [115] use the TG method to analyse fractions of liquefied solid fuels. Atanassov et al. [116] have performed thermal analysis on butylated coal with increased solubility in organic solvents. Handoo et al. [117] seek a connection between the thermal parameters of petroleum waxes and their composition. Savaya et al. [118] use the DSC curves for five products of the vacuum distillation of oil to determine their stability.

CONCLUSIONS

A survey of the literature reveals that differential thermal analysis, as well as thermogravimetric analysis, are finding an increasingly broad application in studying liquid fuels and various petrochemical and coke-chemical products (asphalts, bitumens, resins, waxes, oils, soaps, consistent lubricants, pitches, etc.). These thermal methods are used most frequently in combination with other physical or chemical analyses of the above-mentioned products, which suggests that at least for the time being they do not have an independent importance of their own. In this case the subordinate role of thermal analysis can be explained by the difficulties emerging in the interpretation of the DTA and TG curves obtained. The authors of the publications cited in this survey most frequently find it sufficient to give only a description of the observed endo- and exothermic effects, without being able to explain them unambiguously. This makes it necessary to link thermal analysis even more closely with other modern methods of research. Thermal analysis seems to be particularly useful for studying individual compounds which have a similar composition and a simple structure, and participate as principal components in the different petroleum and coke-chemical products. We have reason to believe that in the years to come this tendency will grow, with the application of thermal analysis to the study of the above-mentioned complex mixtures of hydrocarbons, which additionally contain a larger or smaller percentage of various other compounds.

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