THERMOANALYSIS OF PETROLEUM PRODUCTS CRITICISM TO THE CONRADSON NUMBER AND A POSSIBILITY TO DETERMINE THE FLASH POINT*

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Introduction

From analytical aspects, testing material properties during temperature changes proved to be rather expedient. Continuously developing methods of thermal analysis are, however, applied in other fields than quantitative and qualitative analysis. As against isothermal tests, non-isothermal tests yield a lot of data from a single test. This fact has the quite natural consequence that investigators attempt to determine and understand essentials and kinetics of the involved processes from this type of measurements instead of from more tedious and time consuming isothermal test series. After initial successes, however, these uses of non-isothermal tests turned to complicated problems, to "marshland" — according to the characteristics of kinetical processes. Hence, seemingly well-known compounds considered as safe bases such as calcium oxalate, calcium carbonate, are to be tested as models again and again.

Nevertheless, theoretical and practical analytic work to interpret and apply thermoanalytic phenomena did not meet expectations. Thermal decomposition processes could not be presented by DTA and DTG peak temperatures in a reassuring manner. Peaks became "independent", their temperatures varying as a function of sample volume, heating rate etc. Obviously, with the growth of the number of components, curves soon become confuse, especially for extremely varying compositions. This is the case for testing petroleum products when mostly neither quantity, nor quality of sample components are known separately but ranged into groups established to some or other principle.

For such compounds, thermal processes with rates depending on temperature are overlapping in various ways. It is well-known that distinction of overlapping processes is generally still an unsolved problem. In testing petroleum products, the problem is made more complex by the superposition of the evaporation of systems consisting of many components — known at most by hydrocarbon type groups — to the thermal decomposition processes. This

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fact is responsible for the low number of researchers concerned with the thermal analysis of petroleum products.

Inconsistent results probably due to their complexity seem to be responsible for the unclearedness and debatedness of relevant test conditions. Contradictory opinions are known, for example, about the usefulness of TG distillation curves in connection with the siting of the microdistillating parts of the thermobalance used for analytical purposes and the heating set mounted over it [1—4], or the admixing of solids [5].

Among others, with reference to foaming, it should be noted that evaporation is not the only physical phenomenon which complicates thermal processes.

Possibilities of identifying various thermal processes

Testing of petroleum products has led to the recognition that for getting convincing results partly the fixation of the thermal process has to be attempted and partly thermal decomposition has to be distinguished from evaporation.

Standardization of testing conditions is no solution for fixing the thermal processes. Namely, standardization may help dissimulating causes of phenomena. A more important problem is that for petroleum products it is not possible to keep the sample quantity at a constant value by specifying the weighed quantity alone, because of the variable composition of the sample. Rather than to standardize test conditions, primarily, straightening of thermoanalytic curves has been attempted in application of epistemology results of MILL [6].

VAN KREVELEN et al. [7] succeeded to straighten thermogravimetric curves (TG) by means of the differential equation

$$-\mathrm{d}x/\mathrm{d}t = k(a-x)^n$$

where

$-\mathrm{d}x/\mathrm{d}t$	weight loss rate at temperature T;
$(a-x)$	the concentration of a reactant at time t;
n	reaction order;
k	Arrhenius rate constant depending on the absolute temperature.

Already COATS and REDFERN [8] have indicated their anxiety that this differential equation could hardly be used for any thermal decomposition process. Among others, DRAPER [9] set forth the limitations of its use in detail. Nevertheless, it may be useful, provided that it is not applied beyond its limits. Generally spoken, it is a mathematical tool for transforming measurement data so as to make the thermal process more accessible, more recognizable. There are of course some cases where it can describe the kinetics of the process.

The above statements are illustrated by thermogravimetric test results in Table 1, compiling calcium carbonate test conditions, data [10], as well as reaction order and activation energy values calculated by the method of FREEMAN and CAROLL [11].

Table 1

Effect of sample quantity, heating rate
and crucible shape on DTG peak temperature
and on kinetic constants

Test	Weighed sample mg	Heating rate °C/min	DTG peak °C	Reaction order	Activation energy kcal/mol
1	40	12.6	792	0.25	46.7
2	2000	10.4	947	0.25	51.6
3	200	3.7	825	0.25	43.3
4	200	11.7	870	0.25	36.3
5*	190	1.3	680	0.25	50.8
6**	200	7.5	892	0.0	47.0

* Polyplate sample holder
** Crucible with lid

This table illustrates the often tested and well-known fact that the shape of TG, DTG and for the latter, the peak temperature depend on the sample quantity, the heating rate and other test conditions. Besides, it is also obvious that the reaction order is permanent; it little changed at the fundamental alteration of the character of test conditions. Activation energy ranged about an average value, while DTG peak temperatures differed by as much as 260 °C in extreme cases.

It has to be remembered also that the logarithm of the rate constant as a function of 1/T is expected to be linear, and a different behaviour induces to search for its cause. The quoted differential equation seems to offer a possibility to systematize and survey thermal decomposition processes. Instead of the confusion of curve distorsions due to parameter changes, modification of sample weight, of heating rate etc. offers a deeper insight into the process. The thermal decomposition process is better described by determining the so-called "kinetic constants" than the peak temperature.

In testing petroleum products by thermoanalytic methods, study of the evaporation phenomenon cannot be avoided. It could be stated [12] that when treated by the quoted differential equation, evaporation rate of chemically pure materials invariably appeared to be of zero reaction order, thus, it could be considered as linear function of the reciprocal of temperature. This is to say that for zero apparent reaction order, the possibility of evaporation of chemically pure material has to be reckoned with. There is a strict relationship between equilibrium vapour pressure and evaporation rate at a given temperature.

It was expedient to introduce the notion of fictive evaporation surface expressing the deviation from the equilibrium state during testing. Fictive evaporation surface depends on the temperature, on the composition of the gaseous phase, and is characteristic to the substance.

Testing the evaporation from a mixture gave an unexpected result. Applying the differential equation to this thermal process, partly, the apparent reaction order of evaporation was rather different from zero, as against chemically pure materials, and partly, it much depended on heating rate, as against the thermal decomposition illustrated in Table 1.

Determination of the evaporation from a mixture by means of the common method [11] is rather cumbersome an operation, and the logarithm of the apparent reaction rate constant is no linear function of the reciprocal of absolute temperature — as against most thermal decomposition processes.

According to the presented results, thus, the same formula enables to distinguish between the three phenomena — evaporation of a pure material, evaporation from a mixture, and thermal decomposition — even for an unknown material. This would be impossible from the knowledge of the curves alone, from their shape.

The Conradson number and thermogravimetric testing of the Conradson coke

Determination of the Conradson number is an important standard test in the petroleum industry. Applying to it the statements on thermal decomposition and evaporation, observations can be recapitulated as follows [13].

The Conradson number expresses the percentage by weight of Conradson coke developing when the tested petroleum product is heated in a space-excluding combustion, it being the solid product of quite a series of thermal processes. It can be preassumed that, by tracing decomposition processes, a correlation can be found between some characteristic thermogravimetric data and the Conradson number, lending a basis for the exact determination of the coke residue, in a less empirical manner.

Twelve different substances with Conradson numbers of 3.5 to 17.6 per cent, have been subjected to thermogravimetric analyses in a P.P.E. derivatograph [14].

Various fuel oils have been demonstrated to have peculiar DTG curves [15]. Such a simplified, generalized DTG curve is shown in Fig. 1. The peak traced with a dashed line appears if the fuel oil contains some light hydrocarbon, e. g. petroleum or gas oil. The other peaks are due to thermal decompo-

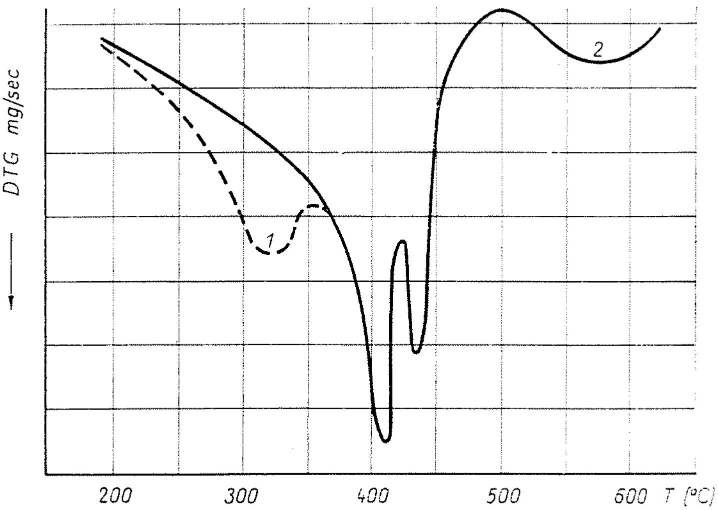

Fig. 1. Simplified DTG curves for fuel oils

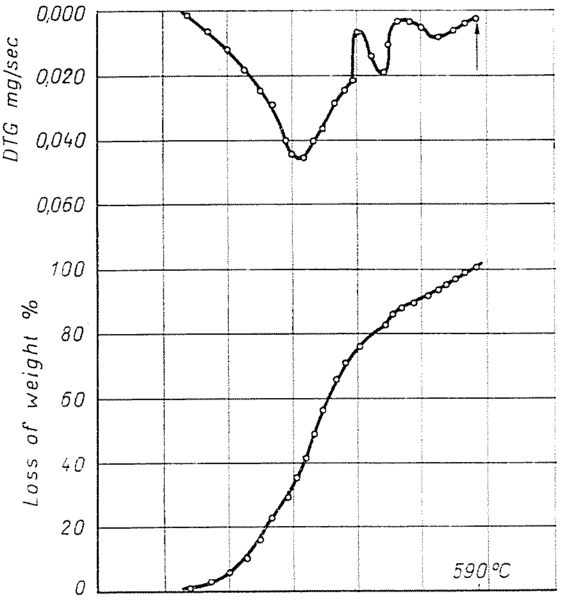

Fig. 2. TG and DTG curves for sulphur-free light fuel oil. Conradson number 4.6%, related temperature 590 °C

sition accompanied by weight loss. For the Conradson number, peak 2 in Fig. 1 is of importance, appearing in the range 475 to 610 °C and for some DTG curves it seems even without kinetic analysis to be the result of several processes. This temperature range includes the decomposition point for the Conradson number that cannot, however, be co-ordinated neither to the beginning, nor to the end point or any other characteristic point of the peak. DTG and TG diagrams of some tested substances indicate the temperature

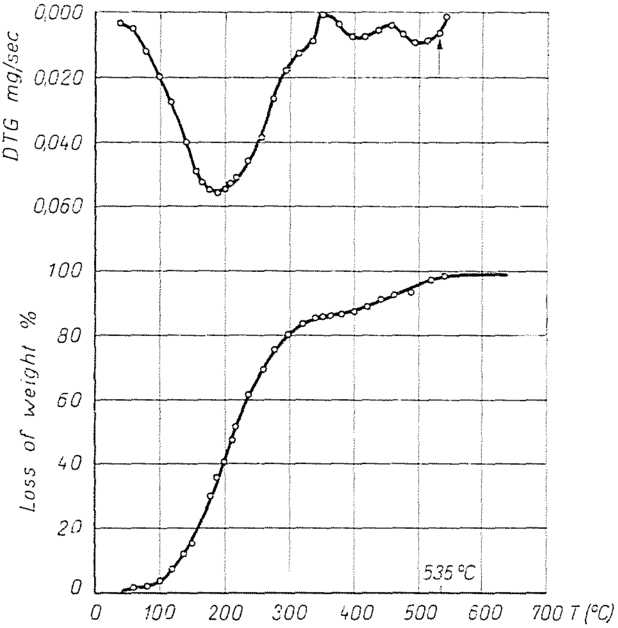

Fig. 3. TG and DTG curves for a light fuel oil (about 30% gas oil, 70% DT-1 Soviet artificial oil), Conradson number 3.5%, related temperature 535 °C

where the weight of material that remained in the crucible in thermogravimetric measurement is equivalent to the Conradson number (Figs 2 through 7).

The Conradson number determined according to the standard method appears to pertain to a peculiar thermal decomposition section but even so, it cannot directly be determined by thermogravimetry. On the basis of thermogravimetric knowledge it is obvious that this can be attributed to shortcomings of the method of determining the Conradson number.

Presented data show that the point in DTG curves equivalent to the Conradson number is related at random to sections of different rates of complex thermal decomposition processes concomitant to weight loss. Hence, determination of the Conradson number means the interruption of a characteristic group of processes in a section of undefined rate and the freezing of

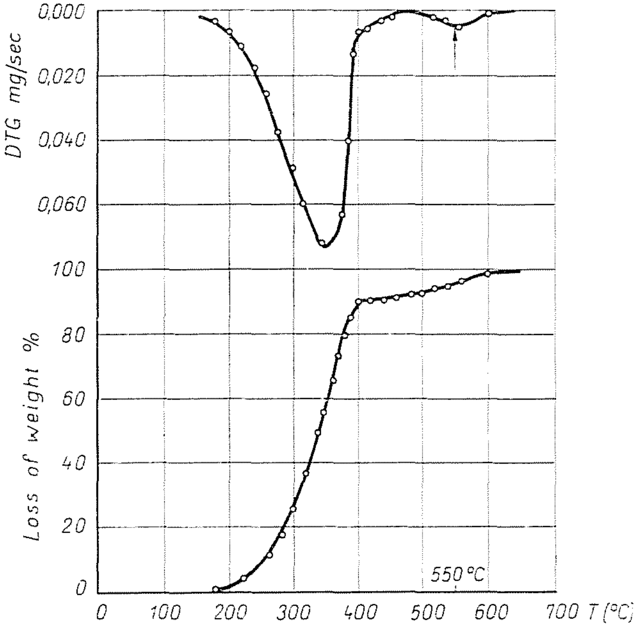

Fig. 4. TG and DTG curves of pure paraffin distillate from Nagylengyel crude. Conradson number 5.4%, related temperature 550 °C

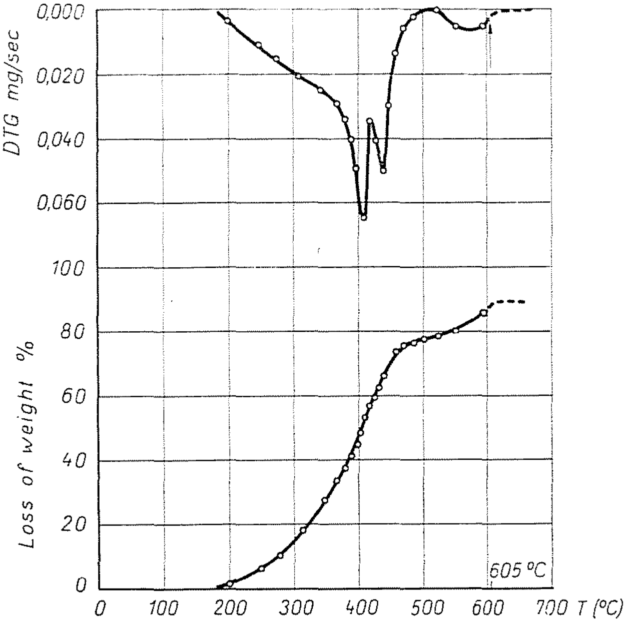

Fig. 5. TG and DTG curves for goudron. Conradson number 15.4%, related temperature 605 °C

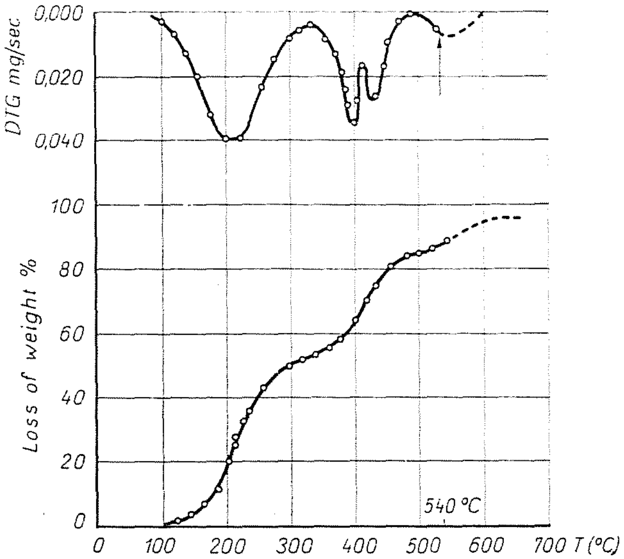

Fig. 6. TG and DTG curves for common fuel oil (about 45% bitumen, 55% gas oil from Lispe). Conradson number 12.7%, related temperature 540 °C

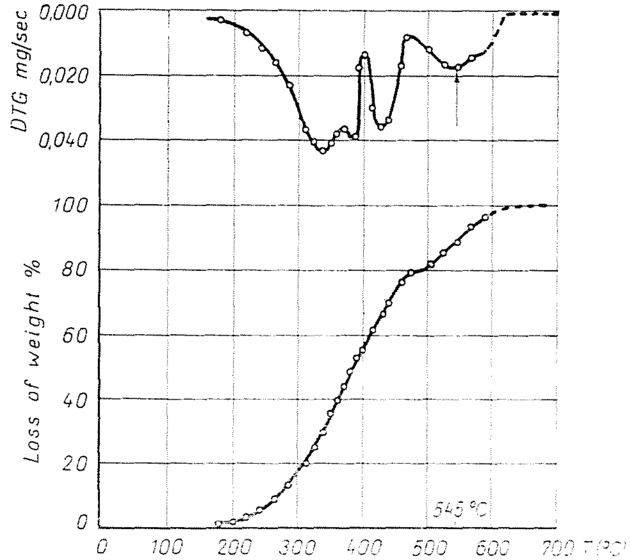

Fig. 7. TG and DTG curves of sulphuric light fuel oil (about 85% mazout, 15% mixed diluting material). Conradson number 12.7%, related temperature 545 °C

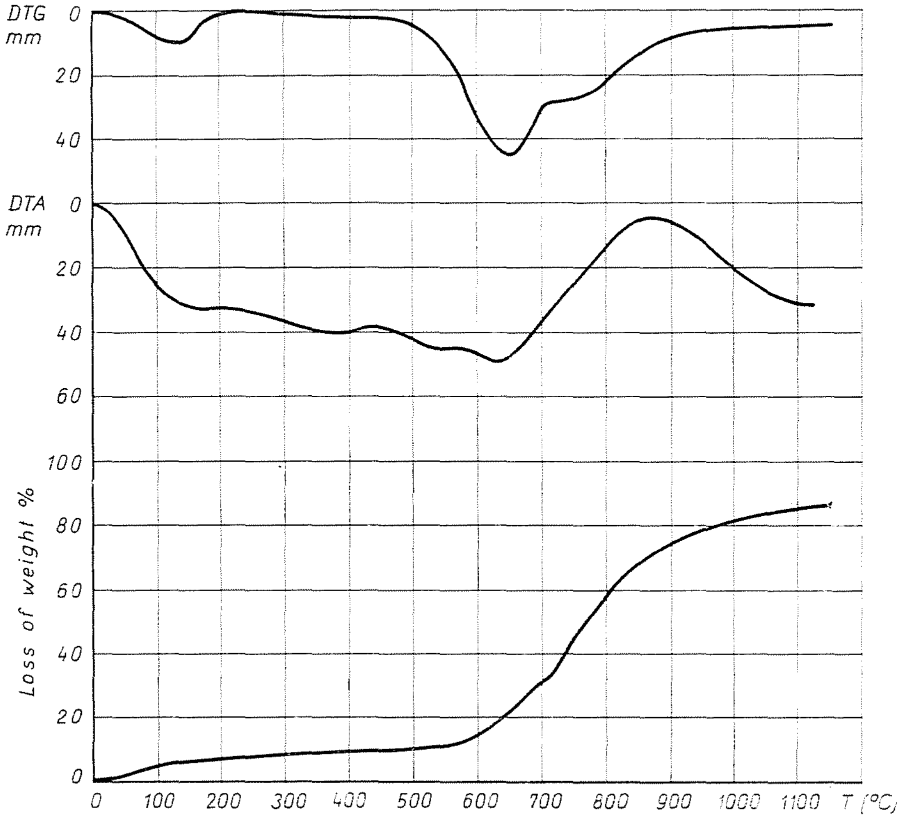

Fig. 8. TG, DTG and DTA curves for Conradson coke

reactions, instead of fixing some state previous to or following some thermal decomposition process. Thus, Conradson number is an ill-defined value, since it depends in an uncertain manner on factors governing the rate of reactions producing the Conradson coke, and is also a function of factors acting at the interruption of reactions.

Thermogravimetric analysis of Conradson cokes from eight different substances under lid, in nitrogen atmosphere, proves that the material evolving at the determination of the Conradson number is a product of incomplete thermal process. TG, DTG and DTA curves of one sample are shown in Fig. 8, those of the others being of the same character.

Curves presented for the sake of illustration (Fig. 8) demonstrate the Conradson number to issue from a non-complete thermal process. It is unexpected to see a weight loss between 100 to 200°C apparent from the DTG curve, although the substance formed at or over 500°C. Evidently, this weight loss is due to desorption, evaporation process, rather than to thermal decomposition. Formation of the so-called Conradson coke is accompanied by the condensation of part of light hydrocarbons present in the air-free space, adding to the Conradson number, the poor definition of which being again apparent from this phenomenon.

In any case, the second DTG peak is a complex resultant of several thermal processes. This fact is obvious from calculations by the CHATTERYÉE method [16] using the already presented differential equation.

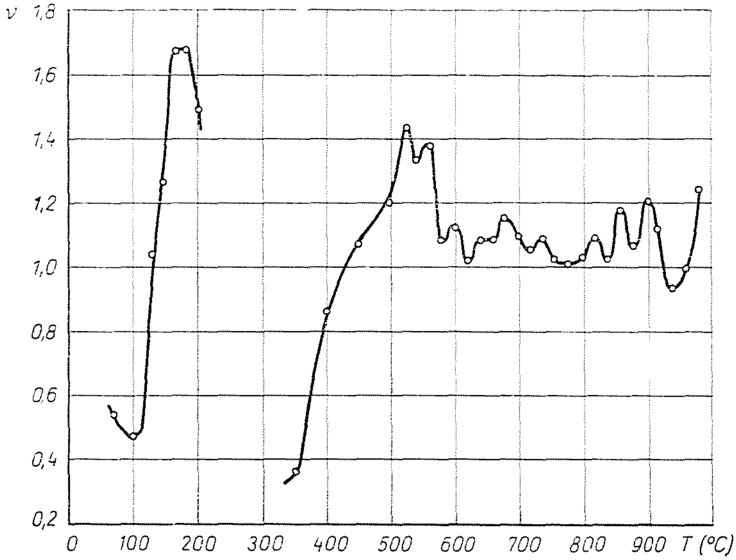

Fig. 9. Temperature dependence of reaction order as calculated from TG and DTG values of Conradson coke, assuming a single thermal process to exist

According to this differential equation, the reaction order is constant for a single thermal decomposition process. Attributing the weight loss of the so-called Conradson coke in the temperature range 70 to 1000 °C to a single process, calculated reaction orders vs. temperature are shown in Fig. 9. These calculations show the weight loss to result from several decomposition processes.

Calculated reaction orders for ranges 40 to 160 °C, 530 to 680 °C and 680 to 860°C are shown in Figs 10, 11 and 12.

For the 40 to 160°C temperature range, the character of the change of reaction order reminds of evaporation from a mixture. Knowing the agent applied for testing, this claims for the statement that the first DTG peak is due to other than thermal decomposition. (Thus, it can be stated that one result of the calculations is the possibility of distinction between weight losses

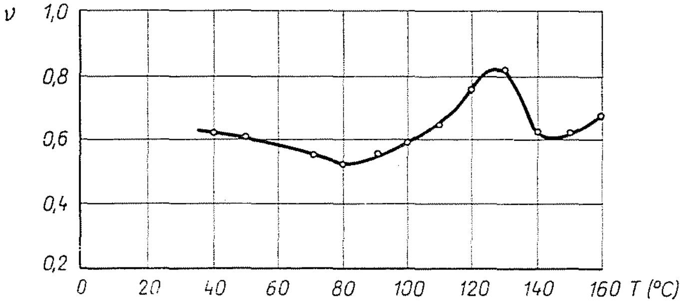

Fig. 10. Temperature dependence of reaction order as calculated from TG and DTG data of Conradson coke in the 40 to 160 °C range

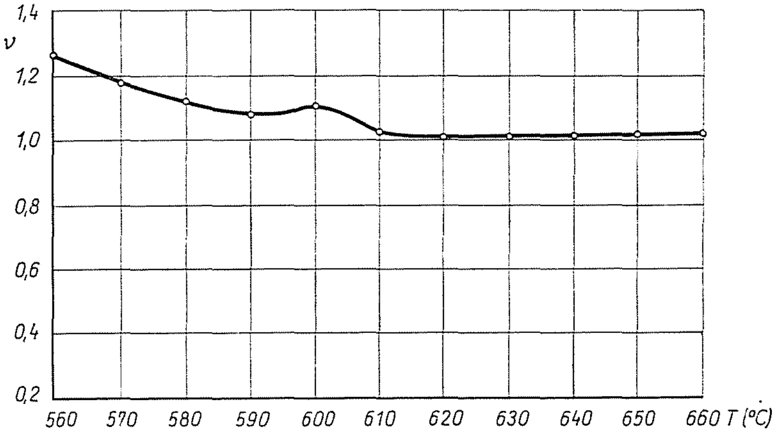

Fig. 11. Temperature dependence of reaction order as calculated from TG and DTG data of Conradson coke in the 530 to 680 °C range

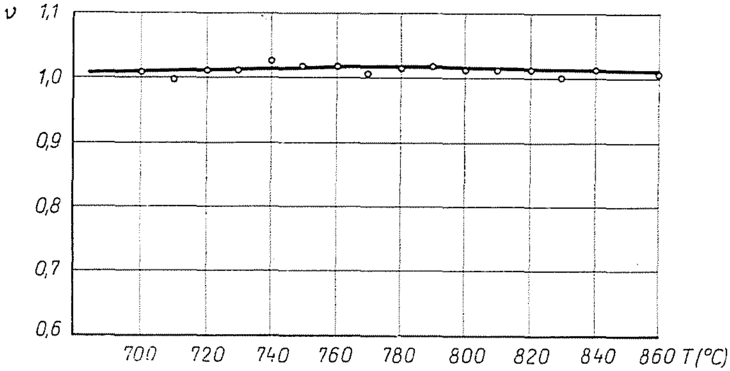

Fig. 12. Temperature dependence of reaction order as calculated from TG and DTG data of Conradson coke in the 680 to 860 °C range

due to thermal decomposition and to other processes. This is impossible if only curve shapes are known.)

Fig. 11 presenting the 530 to 680 °C range indicates there two thermal decomposition processes. The second is not disturbed by overlapping in the range 610 to 660 °C. Reaction order of this process is 1, activation energy being 36.5 kcal/mole.

Decomposition process in the range 680 to 860 °C, is a single process without any overlapping (Fig. 12). This decomposition is also of order 1, the activation energy is 25.1 kcal/mole in the 730 to 780 °C range.

Determination and comparison of weight losses of different Conradson cokes in temperature intervals belonging to each decomposition process leads to the conclusion that the prime material quality is strictly related to three processes in the 400 to 680 °C range, dependent on the chemical composition of the sample applied for determining the Conradson number.

The presented results seem to be sufficient to demonstrate that systematic thermoanalyses and kinetic calculations yield much more valuable knowledge of petroleum products such as fuel oil than determination of the empirical, undefined Conradson number does.

Consequently, though for the time being the industry cannot renounce the use of the Conradson number because of the experience available, anyhow it is worth while to complete the determination of the Conradson number by thermogravimetric tests. It is advisable to indicate residual percentages at the end of thermal processes leading to the so-called Conradson coke and at the end of its decompositions (higher and lower than the standard Conradson number, respectively). Inasmuch as temperatures belonging to the percentages by weight are indicated, thermal tests are to be standardized.

Thermogravimetric flash point determination

Another important standard test to rate petroleum products is the determination of the flash point (ignition point). Thermogravimetry lends itself to this aim.

In flash point determination, a certain quantity of hydrocarbons got upon thermal effect into the gas space has to be mixed with air to produce flash. Hydrocarbon content of the gas space is proportional to the vapour pressure of the test material. In conformity with those stated in the introduction, vapour pressure and weight loss rate are strictly related, therefore it seemed expedient to find a correlation between the logarithm of weight loss rate and the flash point. In the log. DTG vs. 1/T diagram indicating the recorded flash points, these latter are connected by a straight line. Temperatures at the intersection of this straight line and the log. DTG vs. 1/T curves of each sample are compared to standard flash points in Table 2.

Table 2 exhibits a strict correlation between thermogravimetric data and flash points. According to tests in nitrogen atmosphere and with polyplate sample holder, this corrrelation is greatly affected by the gas atmosphere and the crucible shape, without affecting its strictness. Thus, thermogravimetry lends itself both to determine the flash (ignition) point and to describe the combustion properties of the material.

Table 2

Comparison of flash points determined by tests and from diagrams

Sample No.	Flash point, °C	
	Test	Diagram
1	81, 63	80
2	122, 104	112
3	203, 217, 216	217
4	201, 212, 206	211
5	169, 171, 175	149
6	290	268
7	176, 182	170
8	165, 165	171
9	78, 62	69
10	137	147
11	282, 285	293
12	111, 106	105
13	125, 125	148
14	137, 135	143
15	154	163
16	75, 66	82
17	219	221
18	260, 254, 270	265
19	277	276

Further research is needed to refine this method, likely to clear deviations apparent for samples 5,6 and 13 in Table 2. Flash point determined by thermogravimetry can probably be related to the mean molar weight and the chemical group composition of the tested material.

Summary

Thermoanalysis of petroleum products is hampered by the complexity of thermal processes, by physical processes superimposed to the thermal decomposition of multicomponent materials, first of all, by evaporation. Differential equation $-(dx/dt) = k(a - x)^n$ lends itself to distinguish between these processes. Accordingly, apparent reaction order of evaporation of single-component substances is invariably zero, while for mixtures it is non-zero and much dependent on heating rate. In case of thermal decomposition, the reaction order is essentially independent of the test conditions. These findings encourage the use of thermogravimetry for petroleum product testing, what is more, for determining empirical data accessible to standard tests only but of industrial importance. Among these latter, the Conradson number proved to be an ill-defined value. TG and DTG data yield more comprehensive, unambiguous data than are characteristics resulting from the Conradson number. DTG curves help to determine another empiric characteristic of petroleum products viz. flash point (ignition point).

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