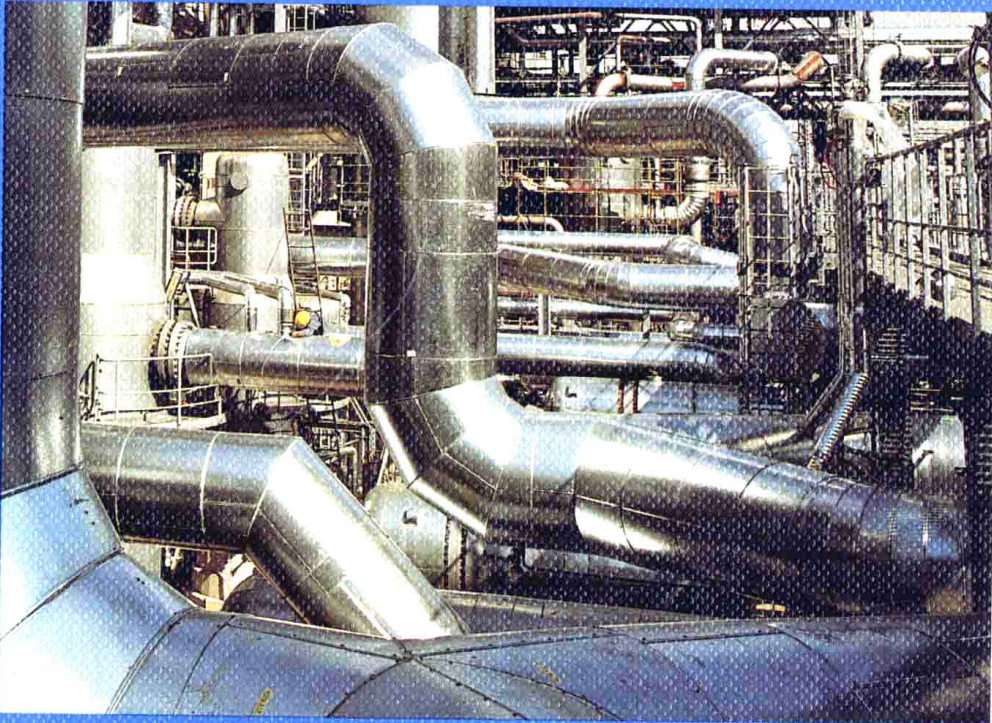Heinz Kopsch

Thermal Methods in Petroleum Analysis

VCH

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in Petroleum Analysis

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Preface

The monograph Thermal Methods in Petroleum Analysis is based mainly on results of more than twelve years research work on the application of thermoanalytical methods to petroleum and its products during the activities of the author at the German Institute for Petroleum Research. It was very interesting to research the application of well defined physical methods, such as thermogravimetry and differential scanning calorimetry, to the multicomponent systems of petroleum and its products, and to understand the limits of those methods on the one hand and the excellent transferability of the results to technical processes on the other. The diversity of possible applications of thermoanalytical methods to various problems in the petroleum laboratory can only be indicated in this monograph.

Many people supported my work, either by active or by indirect help. Thanks are expressed to Mrs. Elvira Falkenhagen, who has been a skilful and reliable assistant for many years, as well as to Dr.-Ing. Maria Nagel, Dr.-Ing. Ulrike Tietz, Mrs. Liliane Varoscic, Mrs. Regina Bosse, Mrs. Gerda Sopalla, and the late Mrs. Heidi Gottschalck. An acknowledgement should be made to the directors of the German Institute for Petroleum Research: Professor Dr. H. H. Oelert, Professor Dr. H.-J. Neumann, and Professor Dr. D. Kessel who granted me maximum independent research capacity. Some parts of the research work were carried out with financial support from the German Association for Research CD (Deutsche Forschungsgemeinschaft). For several years successful and pleasant cooperation was established with colleagues of the University of Belgrade, especially with Professor Dr. D. Skala, Professor Dr. M. Sokic, and Professor Dr. J. A. Jovanovic. Thanks are also expressed to those whose names do not appear in this list. All the companies which supplied me with information as well as with illustrations are likewise acknowledged; their names may be found in the appendix.

I hope that this monograph will be of some help to colleagues in both academic and industrial research establishments and will encourage them towards further attempts in the application of thermal methods of analysis, even to chemically non-defined multicomponent systems. The examples presented might represent a stimulation for further experimental work.

Heinz Kopsch
Oktober 1995

Contents

List of Symbols

A	Frequency or Pre-exponential Factor (min^{-1})
AR	Atmospheric residue
ASTM	American Society for Testing and Materials
BP	Boiling Point ($^{\circ}$C)
CCR	Conradson Carbon Residue (%)
CR	Crackable part of the sample (%)
DDK	Dynamic Difference Calorimetry (see DSC)
DIN	Deutsches Institut für Normung e. V. (German Institute for Standardization)
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
DTG	Differential Thermogravimetry (First differential quotient of weight loss with respect to time) (% min^{-1})
E	Activation Energy (J $\cdot$ Mol^{-1})
e	Base of natural logarithm
exp	Exponent with base e
G_W	Residual weight at the point of inflexion of the TGA curve (%)
H	Energy flow (μW)
H_e	Enthalpy of pyrolysis (J $\cdot$ g^{-1})
H_f	Heat of fusion (J $\cdot$ g^{-1})
H_v	Heat of vaporization (J $\cdot$ g^{-1})
IR	Infrared Spectroscopy
k	Reaction (Rate) Constant (min^{-1})
ln	Natural logarithm
log	Decimal logarithm
$\overline{M}$	Mean relative particle mass (Mean molecular weight)
MP	Melting Point ($^{\circ}$C)
ND	Non-distillable part of the sample (%)
NMR	Nuclear Magnetic Resonance Spectroscopy
n	Reaction order (dimensionless)

P	Pressure (bar)
PCR	Practical thermal crackable part of the sample (%)
Pen	Needle penetration at 25 °C (0.1 mm)
PMB	Polymer modified Bitumen
Q	Quotient of weight loss in air divided by weight loss in inert gas (Isothermal Gravimetry)
R	Universal Gas Constant (J Mol^{-1} K^{-1})
$R600$	Residue (%) at 600 °C experimental temperature
$R800$	Residue (%) at 800 °C experimental temperature
r	Coefficient of correlation (dimensionless)
SAR	Simulated atmospheric residue (%)
S.P.R&B	Softening Point Ring and Ball (°C)
STA	Simultaneous Thermal Analysis (or Analyzer) (TGA+DTA or TGA+DSC)
SVR	Simulated vacuum residue (%)
s	Standard deviation
T	Temperature (Generally °C, except kinetics with absolute temperature K)
TA	Thermal Analysis
T_{Crack}	Start temperature of the thermal crack reaction (°C)
TGA	Thermogravimetry
T_{max}	Temperature of peak maximum (°C)
T_{onset}	Onset temperature (°C)
T_W	Temperature of the point of inflexion of the TGA curve (°C)
$T1\ \%$	Temperature (°C) at 1 % weight loss
$T5\ \%$	Temperature (°C) at 5 % weight loss
t	Time (min)
$t_{1/2}$	Half life time (min)
U	Conversion (%)
V	Coefficient of variation (%)
VR	Vacuum residue
VVR	Visbreaker residue
$\bar{x}$	Arithmetic mean
α	Fractional conversion (dimensionless)
β	Heating rate (K min^{-1})
δ	Solubility parameter according to Hildebrandt ($\sqrt{MJ}$ m^{-3})
Δ	Difference
$\Delta G100$	Weight loss up to 100 °C (%)
$\Delta G200$	Weight loss up to 200 °C (%)
$\Delta G300$	Weight loss up to 300 °C (%)
$\Delta G400$	Weight loss up to 400 °C (%)

1 Introduction

Analytical methods describing the thermal behavior of substances during programmed temperature changes, like thermogravimetry, differential thermoanalysis, or differential scanning calorimetry are old methods, which were applied at first to problems of inorganic chemistry, mainly to minerals. The analysis of petroleum and petroleum products has been mentioned relatively late. In the literature survey by Weselowski [1-1] the first citation dates from 1958. Also, the oldest citation in the research report by Kettrup and Ohrbach [1-2] dates from 1965.

Petroleum, especially heavy crudes, is recovered sometimes by the use of thermal processes like steam flooding or by in situ combustion. The processing of the recovered crudes in the refineries is usually done by thermal methods at very different temperatures. A review of the temperatures applied in refinery operations is given in Table 1-1. These thermal processes are performed partly by sequential heating until the desired products are obtained. The operating parameters for the different processes have been obtained to a large extent by empirical experience or partly by simulation of the processes in laboratory installations or in pilot plants. For that reason thermoanalytical methods are considered to be very useful in obtaining data concerning the thermal behavior i. e. data describing the

Table 1-1: Temperature Ranges in Petroleum Processing

Process	Temperature Range (°C)
Atmospheric Distillation	350 ... 380
Vacuum Distillation	350 ... 380
Thermal Cracking	400 ... 650
Catalytic Cracking	450 ... 540
Steam Cracking	650 ... 1000
High Temperature Pyrolysis	1000
Hydrocracking (Gas Phase)	340 ... 430
Hydrocracking (Liquid Phase)	340 ... 470
Visbreaking	460 ... 480
Reforming (Thermal Treating)	510 ... 580
Reforming (Catalytic Treating)	500 ... 550
Isomerization	60 ... 200
Alkylation (Catalytic)	0 ... 200
Polymerization	170 ... 215
Hydrotreating	250 ... 430
Steam Reforming	700 ... 800
Bitumen Blowing	230 ... 300

thermal and oxidation stability of petroleum and its products; data predicting the manner and quantity of products gained in the processes; and data concerning reaction kinetics which can be used to optimize the refinery processes.

Thermogravimetry (TGA), differential thermoanalysis (DTA), and differential scanning calorimetry (DSC) are the main methods which can be used in the analysis of petroleum and its products. DSC is preferred to DTA, because DSC supplies values of energies directly, whereas the DTA supplies only temperature differences.

These thermal methods of analysis have been described in several basic books [1-3 to 1-17]. The application to polymers is described likewise [1-18, 1-19]. So far no compilation on the application to petroleum and its products exists. The situation in the field of standards is similar. The Normenausschuß Materialprüfung im Deutschen Institut für Normung (Committee for Testing and Materials of the German Institute for Standardization e. V., DIN) has approved only two standards (one of them contains terms of thermal analysis [1-20], the other is the standard for thermogravimetry [1-21]). Furthermore there are three proposals (principles of differential thermal analysis [1-22], determination of melting temperatures of crystalline material by DTA [1-23], and testing of plastics and elastomers by DSC [1-24]). The American Society for Testing and Materials (ASTM) has to date approved forty standards for the application of thermal methods of analysis. Among them, seven standards are concerned with the testing of petroleum and its products [1-25] to [1-32], six standards are general methods [1-32] to [1-38], and four standards concerning the testings of polymers are applicable to petroleum and its products too [1-39] to [1-42].

2 Methods and instrumentation

Using thermogravimetry (TGA), the dependence of the change in sample weight (mass) on the temperature during programmed temperature changes in a chosen gas atmosphere can be measured. The first derivative of the weight (mass) signal with respect to time is called derivative thermogravimetry (DTG) and is a criterion for the reaction rate. It is usual to record both the slope of the weight (mass) versus the time or temperature (TGA), and the differentiatoed curve versus the time or temperature (DTG). The heating rate dictates the actual position of the TGA and DTG graphs; it is therefore advisable always to use the same heating rate (β) so that different tests may be compared. For small sample weights (masses), up to approximately 10 mg, a standard heating rate of 10 K/min is practicable. This heating rate is slow enough to avoid any temperature gradient inside the sample while permitting a reasonable utilization of the available working time. The shift to higher temperatures of the TGA and DTG curves as a consequence of faster heating rates permits calculation of the Arrhenius kinetic parameters and hence investigation of the reaction kinetics (see chapter 3.3). Furthermore, the position of the TGA and DTG curves will be influenced by the shape of the sample pan, especially by the ratio of surface to volume of the sample, and lastly by the quantity of gas flowing through the oven (gas flow rate). Therefore it is important that variations in sample quantity are minimized and that the gas flow rate is maintained as constant as possible. However, the gas flow rate must not fall below a certain minimum value in order to avoid condensation of evaporated sample fractions on the hangdown of the sample holder or in the gas outlet tubes. The minimum gas flow rate depends on the geometric shape of the oven and the position of the gas inlet and outlet tubes and therefore differs for different instruments. If the gas flow rate is sufficient, the evaporated portions of the sample will be discharged immediately and therefore no equilibrium between liquid and vapor will be attained. As a consequence the boiling (evaporation) temperature of the sample will decrease adequately. That can be used to perform a simulated distillation (see chapter 3.1.2). However, the application of thermoanalytic methods is limited to substances having a start temperature of evaporation at atmospheric pressure not far below 200 °C. Otherwise there is the risk that evaporation in the gas flow will begin at room temperature and thus the correct start temperature of evaporation (zero point of the TGA curve) cannot be ascertained.

In principle all except very corrosive gases can be passed through a thermobalance; in practice the inert gases nitrogen, helium, and argon and the reactive gases air, oxygen, and hydrogen will be used.

The weight calibration of thermobalances is done using standard weights. The temperature calibration is more difficult. The method using the Curie point temperature, as

described in ASTM E 914-83, does not work if a magnetic field from outside the oven is prevented from reciprocal action with the standard inside the oven, by the construction or the material of the oven. Calibration using calcium oxalate monohydrate for standard is very common, since it has exhibited three clearly-defined steps of weight loss during heating (Fig. 2-1 to 2-3).:

Reaction		Temperature Range at β= 10 K/min (°C)	Residue (%)	DTG Maximum Temperature (°C)
$CaC_2O_4 \cdot H_2O$	$\rightarrow CaC_2O_4 + H_2O\uparrow$	135 . . . 175	87.7	163
CaC_2O_4	$\rightarrow CaCO_3 + CO\uparrow$	463 . . . 502	68.5	491
$CaCO_3$	$\rightarrow CaO + CO_2\uparrow$	660 . . . 740	38.4	722

As can be seen from the figures, the DTG maximum is found at conversions which are smaller than the maximum conversion of the reaction step concerned. The onset temperatures as well as the DTG maximum temperatures can be reproduced with coefficients of variation < 2 % of the corresponding mean value.

The thermogravimetric experiments are run using open platinum sample pans. Pans made from aluminium, platinum, quartz, glass, stainless steel etc. were also available. The
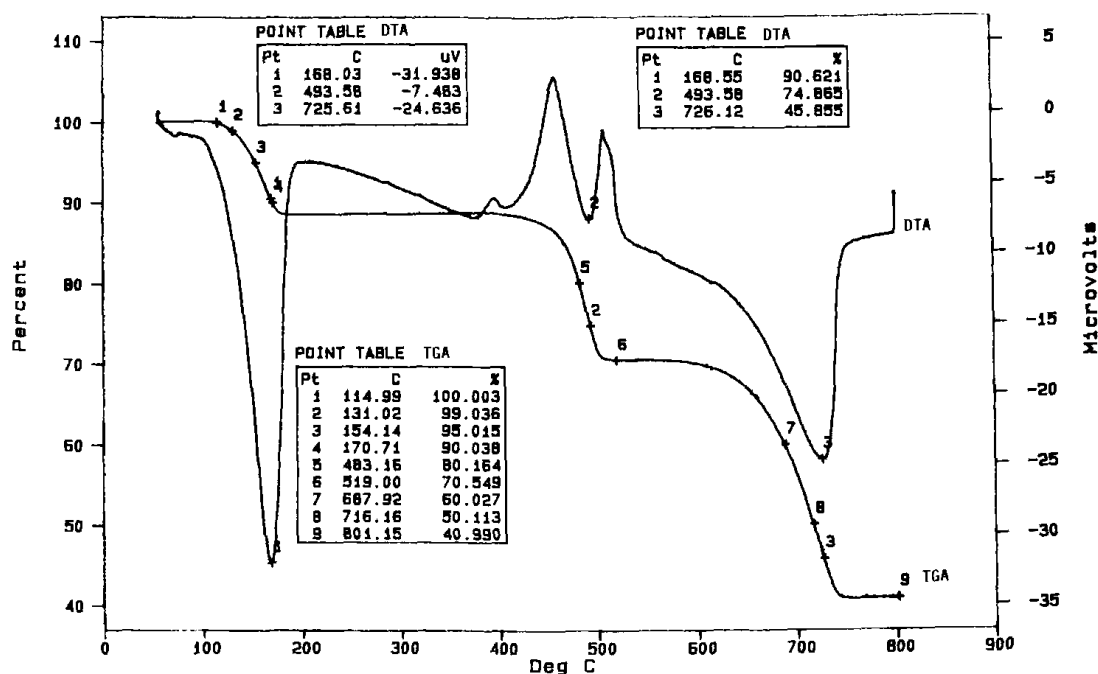

Fig. 2-1: Thermogravimetry of $CaC_2O_4 \cdot H_2O$
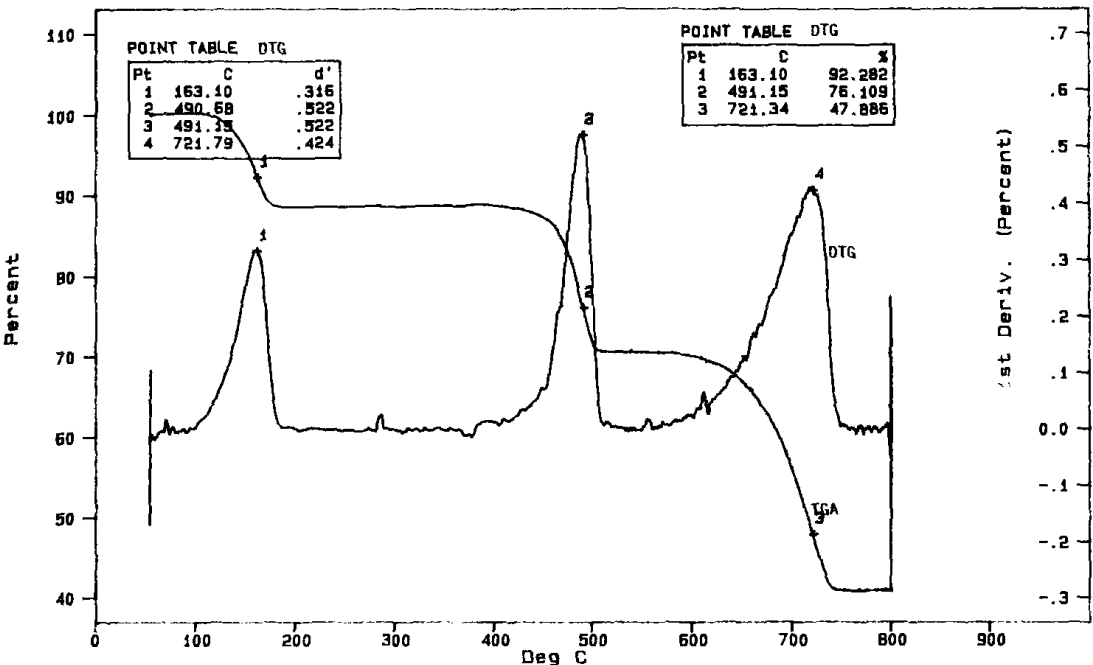Plot of STA 780: TGA and DTA
Atmosphere: Argon 30 + 20 cm³/min
Heating Rate β: 10 K/min

Fig. 2-2: Thermogravimetry of $CaC_2O_4 \cdot H_2O$
Plot of STA 780: TGA and DTG
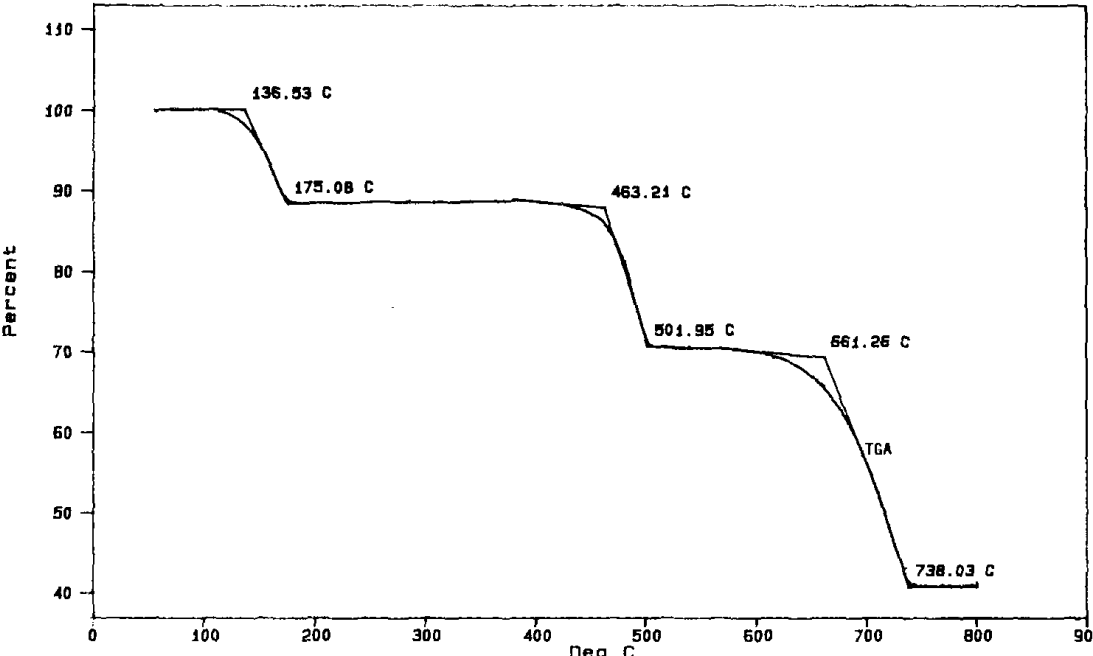Atmosphere: Argon $30 + 20$ cm^3
Heating Rate β: 10 K/min/min

Fig. 2-3: Thermogravimetry of $CaC_2O_4 \cdot H_2O$
Plot of STA 780: onset point and offset point temperatures of TGA
Atmosphere: Argon $30 + 20$ cm^3/min
Heating Rate β: 10 K/min