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PYROLYSIS ANALYSIS AND KINETICS OF CRUDE OILS

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Abstract

This research presents the results of an experimental study on the determination of pyrolysis behaviour and kinetics of six crude oils by differential scanning calorimetry (DSC) and thermogravimetry (TG/DTG). Crude oil pyrolysis indicated two main temperature ranges where loss of mass was observed. The first region between ambient to 400°C was distillation. The second region between 400 and 600°C was visbreaking and thermal cracking. Arrhenius-type kinetic model is used to determine the kinetic parameters of crude oils studied. It was observed that as crude oils gets heavier (°API decreases) cracking activation energy increases. Activation energy of cracking also show a general trend with asphaltene content.

Keywords: crude oil, differential scanning calorimetry, kinetics, pyrolysis, thermal analysis, thermogravimetry

Introduction

In recent years the application of TG and DSC to study the pyrolysis behaviour of fossil fuels has gained a wide acceptance among research workers, which is exceptional significance for industry and for economy. Ranjbar and Pusch [1] studied the effect of the oil composition, characterised on the basis of light hydrocarbon, resin and asphaltene contents, on the pyrolysis kinetics of the crude oils. The results showed that the colloidal composition of oil as well as the transferability and heat transfer characteristics of the pyrolysis medium have a pronounced influence on the fuel formation and composition. Ranjbar [2] investigated the influence of reservoir rock composition on the pyrolysis and combustion behaviour of crude oils in porous media. He concluded that clay minerals present in matrix, enhance fuel deposition during pyrolysis process and also catalyse the oxidation of fuel. Jha and Verkocy [3] used TG/DTG and DSC on two heavy oil cores, extracted oils and mineral matter in helium and air atmosphere. Their results demonstrated at least three groups of chemical reactions occurring

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in three temperature regimes. Bae [4] investigated the thermo-oxidative behaviour and fuel forming properties of various crude oils. The results indicated that oils can be classified according to their oxidation characteristics. No complete correlation was established between viscosity, composition or density of the crude with the thermooxidative characteristics of crude oils. Drici and Vossoughi [5] applied TG/DTG and DSC to crude oil characterisation in the presence and absence of metal oxides. Vanadium, nickel and ferric oxides behaved similarly in enhancing the endothermic reactions. Kök [6] applied TG/DTG and DSC techniques to characterise the pyrolysis and combustion properties of two heavy crude oils. In pyrolysis experiments, temperature ranges where distillation and cracking occur were identified. Kök and Okandan [7] applied a weighted mean activation method to describe the reactivity and combustibility of crude oils via simultaneous TG/DTG method. The rate data fitted to an Arrhenius equation; the plots showed three distinctive reaction regions. A correlation was established between mean activation energy and °API gravity and peak temperatures during high-temperature oxidation. Philips *et al.* [8] used PDSC for an investigation of the pyrolysis and oxidation of Athabasca oil sands at several pressures. No results were quoted on the effect of sand grain size.

The aim of this research is to identify the pyrolysis behaviour of crude oils by means of DSC and TG/DTG and to determine the kinetic parameters of the samples studied.

Experimental

Six crude oils were tested under pyrolysis conditions with DuPont 951 TG/DTG and 910 DSC equipment's. Differential heat flow of the samples is monitored by DSC whereas TG/DTG has the capability of measuring the mass loss either as a function of temperature or time in a varied but controlled atmosphere. Subsequent to experiments DSC system was calibrated for temperature readings using indium as reference standard. The TG/DTG system was also calibrated for temperature readings with calcium oxalate monohydrate. It was also

Table 1 Properties of crude oils

Crude oil	°API	$<C_{15}$	%SAT	%AROM	%NSO	%ASP
Venezuela	12.2	n.a	n.a	n.a	n.a	n.a
B. Raman	14.9	16.91	18	31	22	29
B. Kozluca	15.8	15.15	18	32	20	30
Raman	19.1	16.32	31	29	19	21
Garzan	26.1	21.81	45	29	14	12
Bulgurdag	36.4	28.02	72	16	9	3

n.a: not available

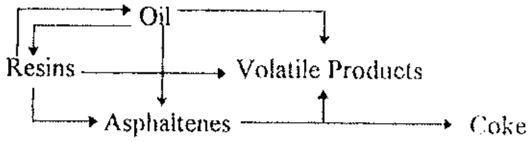
essential to calibrate the balance for buoyancy affects for the quantitative estimation of mass changes. The material chosen for the investigation of such effects was silver. The crude oils used in this research were from Garzan, Raman, B. Raman, Bulgurdag, B. Kozluca and Venezuela oil fields. Properties of these crude oils are given in Table 1. The experimental procedure involves placing 10 mg of sample in a pan, setting the heating rate and flow rate of the purge gas (nitrogen), then commencing the experiment. All experiments were performed at a linear heating rate of 10°C min^{-1} over the temperature range 20–600°C with a nitrogen flow of 50 ml min^{-1}. In order to assess the reproducibility, experiments were performed twice.

Results and discussion

Many hydrocarbon compounds undergo permanent molecular change when subjected to extreme heat. The extent of this change depends on the complexity of the molecular structure of the reaction environment. Endothermic reactions are generally termed as cracking or pyrolysis reactions. In the initial stages of pyrolysis, distillation of low molecular mass species occurs, but as the temperature rises, in addition to the increased rate of volatilisation due to the progressive evaporation of the larger molecules, cracking of compounds may also occur producing volatile fragments.

In TG/DTG pyrolysis experiments mainly two mass loss regions were detected on the curves (Fig. 1). One of these regions is the ‘distillation’ in which mass loss is mainly attributed to distillation where light and medium hydrocarbons are vaporised due to heat effect. In TG/DTG curves this region is characterised as a hump at relatively lower temperatures (up to 650 K). It was observed that extent of distillation or mass loss amount till the severe reactions at higher temperatures are closely related by the amount of saturates in crude oils. Bulgurdag and Garzan crude oils that have highest amount of saturate have highest amount of mass loss till main cracking reaction. On the contrary, B. Kozluca and B. Raman crude oils whose saturate are the lowest, have lowest amount of mass loss in distillation or mild reaction region.

In pyrolysis reactions when temperature is increased to higher values some chemical reactions begin to complete, like visbreaking and cracking through the reaction pathway as suggested by Levinter and Medvedeeva [9].



In this region asphaltene yield begins to increase and coke production starts when asphaltene yield reaches a maximum [10]. The region where cracking/coking reaction occurs is termed as 'cracking' region which is seen as a relatively steep peak in TG/DTG curves. In this region, the C–C, C–H and C–heteroatom bonds are broken producing reactive free radicals. These radicals can either continue their own cracking or con with separation of a low H/C carbonaceous material [11].

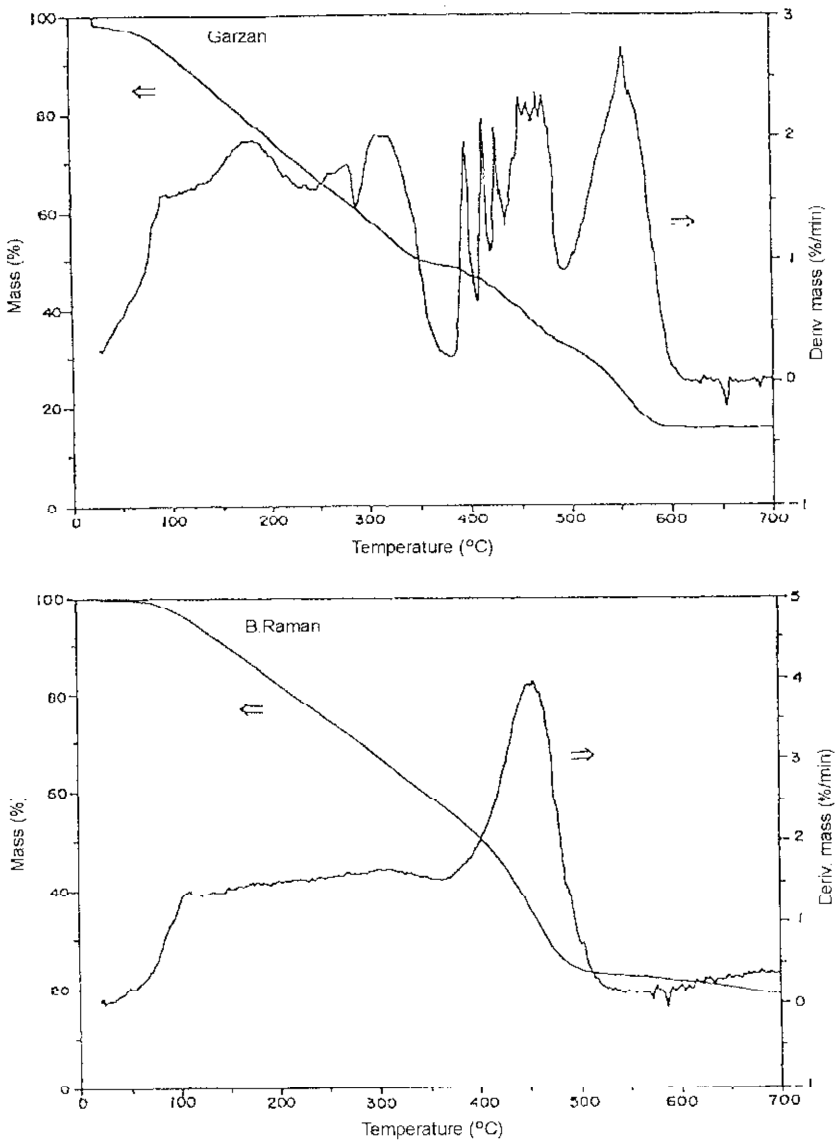


Fig. 1 TG/DTG curves of crude oils

Table 2 TG/DTG results and activation energies (kJ mol^{-1}) of crude oils

Crude oil	Dist.	Crac.	Coke/%	E/kJ mol^{-1}
	mass loss%			
Venezuela	46.44	32.84	21.16	58.9
B. Raman	44.29	33.06	22.65	54.2
B. Kozluca	44.02	32.61	23.39	67.4
Raman	60.86	16.42	22.72	46.2
Garzan	69.65	21.99	8.47	48.1
Bulgurdag	90.56	3.02	6.43	51.2

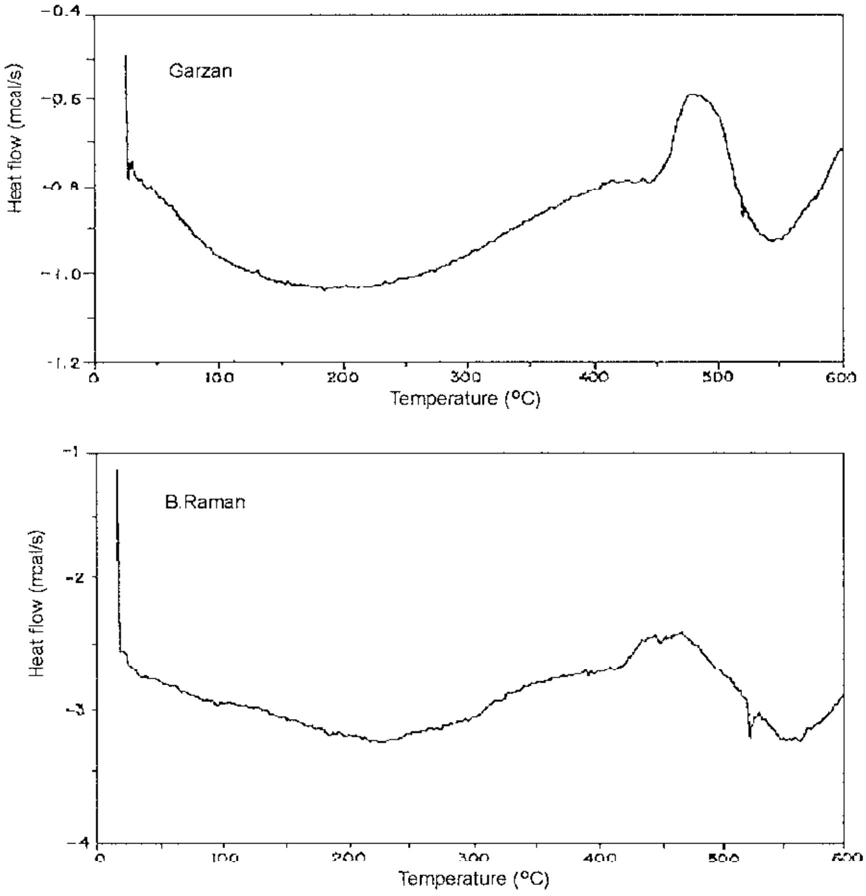


Fig. 2 DSC curves of crude oils

In this study, it was observed that the amount of material consumed in cracking region and the cracking activation energy, calculated using first order Arrhenius model, is dependent on the amount of asphaltenes in crude oil and the heavy nature. When asphaltene content in crude oil increases, material consumed in cracking region also increases. This shows that mostly asphaltene fraction of oil engages in cracking reaction. But coke yields of crude oils is not well correlated with the amount of asphaltenes in crude oils that shows that the structure of asphaltenes is also very important for the efficiency of asphaltene conversion to coke. Moreover, formation of the resultant coke yields higher amount than the asphaltene content in Bulgurdag crude oil suggests that not only the asphaltenes but also other fractions of crude oils (NSO's and aromatics) are responsible for the. resultant coke yield. Numerical results obtained in TG/DTG pyrolysis experiments are given in Table 2.

DSC pyrolysis experiments show the same type of reactions on energy scale in mcal s^{-1} (Fig. 2). DSC curves for both the distillations and cracking reactions show endothermic effects. The calorific value due to cracking reaction is related to the asphaltene content and °API gravity of crude oil. When °API gravity of crude oil decreases and asphaltene amount increases, the heat value of this reaction also increases. This fact can be explained as the crude oils that loose more mass (more material) in cracking region, necessitates more heat flow for the reaction as followed from DSC. Heat amounts of crude oils in cracking region is given in Table 3.

The pyrolysis kinetics of crude oils is extremely complex, but if certain broad generalisations are made, certain useful information can be deduced. Since the sample size is small and there is an excess nitrogen supply, the progress of the reaction is independent of the nitrogen concentration. It is therefore reasonable to assume that the pyrolysis reaction can be described by first-order kinetics from TG/DTG data. Thus, the following relationship holds;

$$dW/dt = kW^n$$

The temperature dependence of k is expressed by the Arrhenius equation,

$$k = A_r \exp(-E/RT)$$

Assuming first-order kinetics (n=1),

$$dW/dt = A_r \exp(-E/RT)W$$

$$dW/dt\ 1/W = A_r \exp(-E/RT)$$

Taking the logarithm of both sides,

$$\log[(dW/dt)\ 1/W] = \log A_r - E/2.303RT$$

where; dW/dt is the rate of mass change of the reacting material, A_r is the Arrhenius constant, E is the activation energy, T is the temperature, R is the gas law constant and n is the reaction order. When $\log[(dW/dt)1/W]$ is plotted against $1/T$, a straight line is obtained will have a slope equal to $E/2.303R$. Linear least square correlation coefficients for the identified rectilinear portions varied from 0.95 to 0.99.

Table 3 Heat of reactions of crude oils

Crude oil	Heat of reaction/cal g^{-1}
Venezuela	42.2
B. Raman	39.5
B. Kozluca	40.3
Raman	22.1
Garzan	14.3
Bulgurdag	2.8

For Bulgurdag crude oil there is no apparent cracking region whose activation energy is to be calculated. For other crude oils, activation energies show a general trend with °API gravity. As crude oils gets heavier (°API decreases) cracking activation energy increases (Table 2). Activation energy of cracking also show a general trend with asphaltene content. Thus, it is concluded that as heavy and resistant components increase in the crude oil, activation energy of cracking show an increase.

Conclusions

A DSC and TG/DTG was used to study crude oil pyrolysis. In TG/DTG pyrolysis experiments mainly two mass loss regions were detected on the curves. One of these regions is the distillation, in which mass loss is mainly attributed to distillation where light and medium hydrocarbons are vaporised due to heat effect. In pyrolysis reactions when temperature is increased to higher values some chemical reactions begin to complete, like visbreaking and cracking. The region where cracking/coking reaction occurs is termed as cracking region which is seen as a relatively steep peak in TG/DTG curves. It was observed that as crude oils gets heavier cracking activation energy inereases. Activation energy of cracking also show a general trend with asphaltene content. DSC curves for both the distillation and cracking reactions show endothermic effects. The calorific value due to cracking reaction is related to the asphaltene content and °API gravity of crude oil.

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