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Use of thermal equipment to evaluate crude oils

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Abstract

A Du Pont differential scanning calorimeter (DCS) and thermogravimetric analyzer (TGA) has been used to characterize the pyrolysis and combustion properties of two heavy crude oils. In pyrolysis runs, temperature ranges where distillation and visbreaking occur were identified. In combustion with air three different reaction regions were identified, known as low temperature oxidation, fuel deposition, and high temperature oxidation. DSC–TGA curves have also been used to determine the heat values and reaction parameters of crude oils.

INTRODUCTION

Thermal processes constitute an important part of enhanced oil recovery techniques. Applying heat to oil reservoirs can result in more efficient oil recovery by fluid drive through viscosity reduction and also scavenging by vaporization, and minimizing the effects of reservoir inhomogeneities. The thermal energy may be introduced from the surface in the form of hot water, oil or gases or as steam. It may also be generated in situ by burning part of the oil in underground reservoirs, a process known as in situ combustion. In situ combustion is a complex process which involves simultaneous heat and mass transfer in a multi-phase environment coupled with chemical reactions of the crude oil combustion. The numerous chemical reactions coupled with simultaneous heat, mass and momentum transfer make in situ combustion one of the most difficult enhanced oil recovery methods. Although much work has been carried out to study the thermal and fluid dynamics aspects of the in situ combustion process, the chemical reaction kinetics remain the least investigated aspect of underground combustion.

Tadema [1] was the first investigator to use thermal analysis techniques to investigate in situ combustion. He showed that DTA curves obtained

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from the combustion of crude oil in the presence of sand consisted of two distinct regions. These two regions were called low and high temperature oxidation (LTO and HTO respectively), and started around 200 and 350°C respectively.

Burger and Sahuquet [2] used DTA to illustrate the catalytic effect of some metallic derivatives and to investigate how the properties of both oil and porous media influence crude oil combustion. They found that heavy metal oxides increased coke deposition and catalyzed the high temperature oxidation reactions.

Bae [3] used TGA and DTA to investigate the thermo-oxidative behaviour of fifteen crude oils ranging from 6 to 38 °API at pressures up to 100 p.s.i. in nitrogen and air. He classified the oils into three categories based upon their oxidative behaviour in TGA at high pressures. No complete correlation could be established between viscosity, composition or density of the crude oil and the thermo-oxidative characteristics of crude oil.

Jha and Verkoczy [4] estimated kinetic and thermochemical data for thermolysis, low temperature oxidation, cracking, coking and combustion reactions in cores and separated oils. The results showed that the oxidation and combustion reaction rates were non-linearly dependent on the heating rates.

Hughes and Price [5] used high pressure differential scanning calorimetry (PDSC) to study the effect of sand particle size, pressure, oxygen partial pressure and carbon dioxide additions on the heat evolution during combustion of heavy oil–sand mixtures. They have observed that decreasing particle size and increase of pressure tended to increase the extent of LTO, thus favouring fuel lay-down.

Vossoughi and Drici [6] applied DSC and TGA to crude oil combustion in the presence and absence of metal oxides. Vanadium, nickel and ferric oxides behaved similarly in enhancing the endothermic reactions. They observed that in the presence of material of large surface area such as with silica, the surface reactions are predominant and are unaffected by the small amount of metal oxide present.

EXPERIMENTAL

Experiments were made using a Du Pont 9900 thermal analysis system with differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA) modules.

Samples

The crude oils used in this present study were from the Turkish oil fields Raman and Bati Raman, with API gravities of 18.7 and 12.9° respectively. Detailed properties of the crude oils are listed in Table 1.

TABLE 1

Properties of crude oils

Crude oil	Temp. (°C)	Specific gravity	°API	Dynamic viscosity
Raman	20	0.9422	18.7	2261
	38	0.9351		421
	50	0.9291		146
Bati Raman	20	0.9799	12.9	51 935
	38	0.9711		6846
	50	0.9632		1830

Procedure

The experimental procedure involves placing 10 mg of sample in a pan, setting the heating rate and flow rate of the purge gas (nitrogen or air), then commencing the experiment. All experiments were performed at a linear heating rate of 10°C min^{-1} over the range 25–600°C with a gas flow of 53 ml min^{-1}. In order to assess the reproducibility, experiments were performed twice.

Prior to the experiments, the DSC system was calibrated for temperature readings using indium as reference standard. The TGA apparatus was also calibrated for temperature readings with calcium oxalate monohydrate. It was essential to calibrate the balance for buoyancy effects to allow quantitative estimation of weight changes. The material chosen for investigating such effects was silver, which has a melting point of 960.8°C.

RESULTS AND DISCUSSION

Runs with a Du Pont differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA/DTGA) were carried out to characterize the pyrolysis and thermo-oxidative behaviour of the crude oils in nitrogen and in air. Kinetic parameters of the crude oils were also calculated from these runs.

Pyrolysis experiments

In the initial stages of the pyrolysis, distillation of low molecular weight species occurs, but as the temperature is raised, in addition to the increased rate of volatilization, cracking of compounds may also occur to produce volatile fragments. In pyrolysis runs, when crude oil was heated in a nitrogen atmosphere, two different mechanisms causing loss of mass were observed (Figs. 1 and 2). The first region between ambient temperature, and 400°C involved distillation. A second region between 400 and 600°C involved visbreaking and thermal cracking.

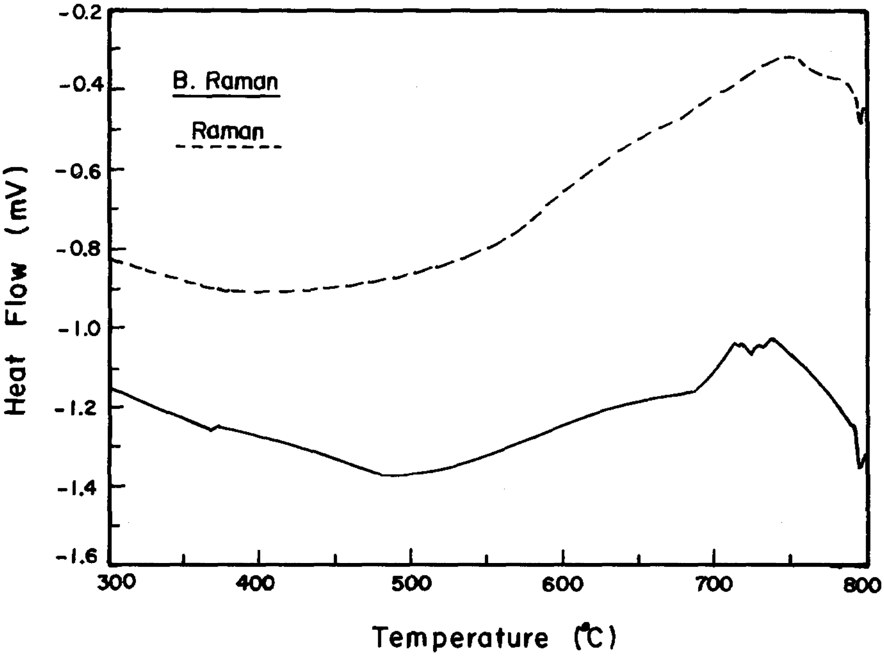

Fig. 1. DSC thermograms of crude oils (pyrolysis).

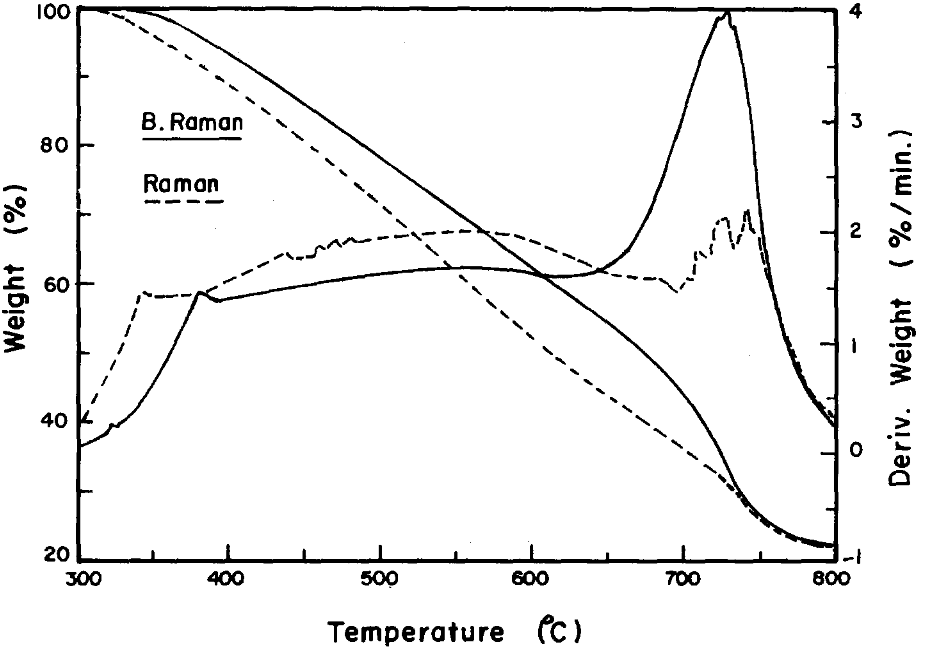

Fig. 2. TGA thermograms of crude oils (pyrolysis).

Combustion experiments

In combustion with air, three distinct reaction regions were identified for both crude oils in TGA/DTGA thermograms. A reaction up to 390°C was actually the first region of the crude oils and is designated low temperature oxidation (LTO). A second transition takes place between 390 and 490°C and is called fuel deposition (FD). The final reaction of crude oil inferred from the thermograms takes place between 490 and 600°C. This reaction contributes most of the exothermic heat of reaction when the crude oil is heated in an oxidizing environment, and is called high temperature oxidation (HTO) (Figs. 3–6).

Under non-isothermal heating conditions, DSC thermograms giving heat flow rates as the material reacts with the flowing gas indicated that the heavy oils were generating high heat flows in HTO regions, which was an indication of high coke content available for combustion. As the crude oil gravity increased, heat released during LTO increased, indicating that more material was available for the reaction. HTO regions occurred at higher temperatures but with lower heat flow rates. The peak temperatures, heat flow rates, the heat evolved during LTO and HTO and the total heat evolved are given in Table 2 as the averages of two runs.

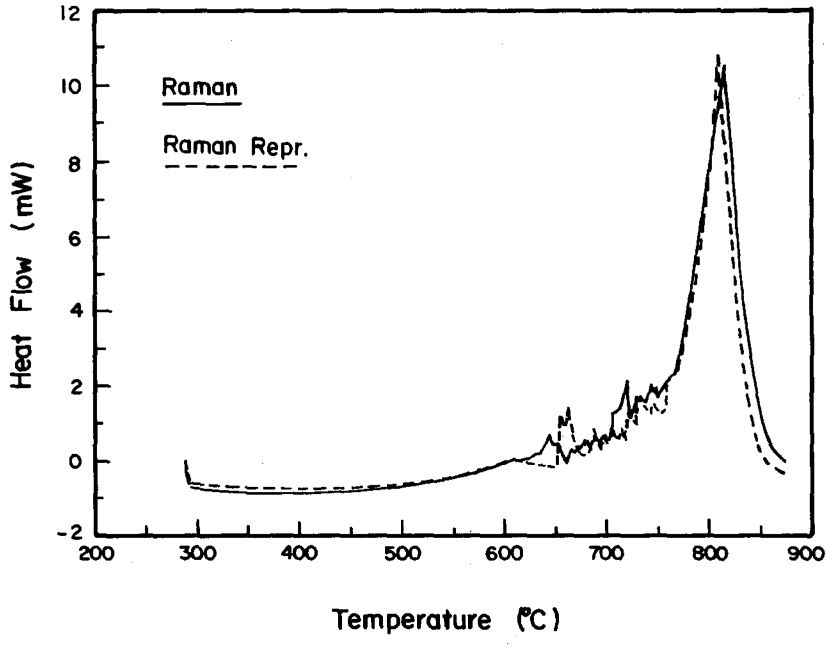

Fig. 3. DSC thermogram of Raman crude oil (combustion).

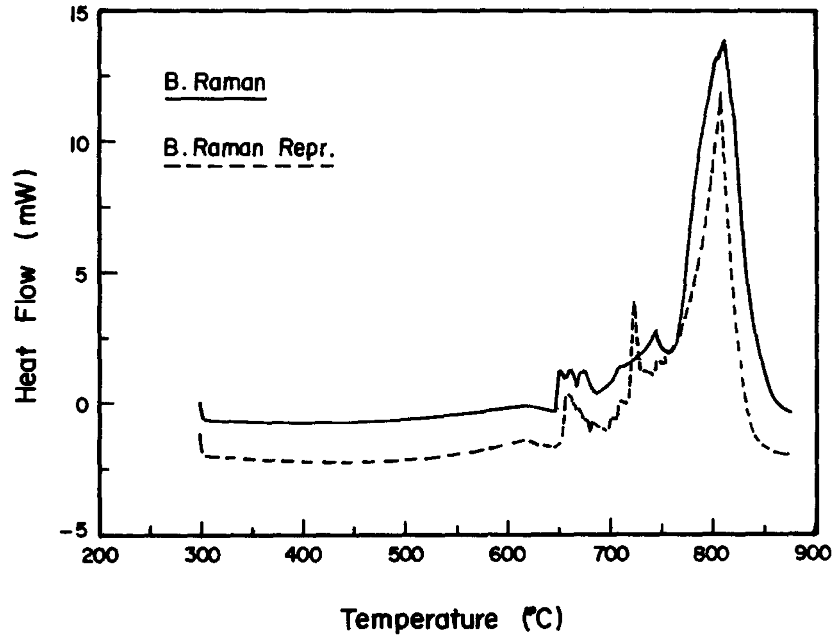

Fig. 4. DSC thermogram of Bati Raman crude oil (combustion).

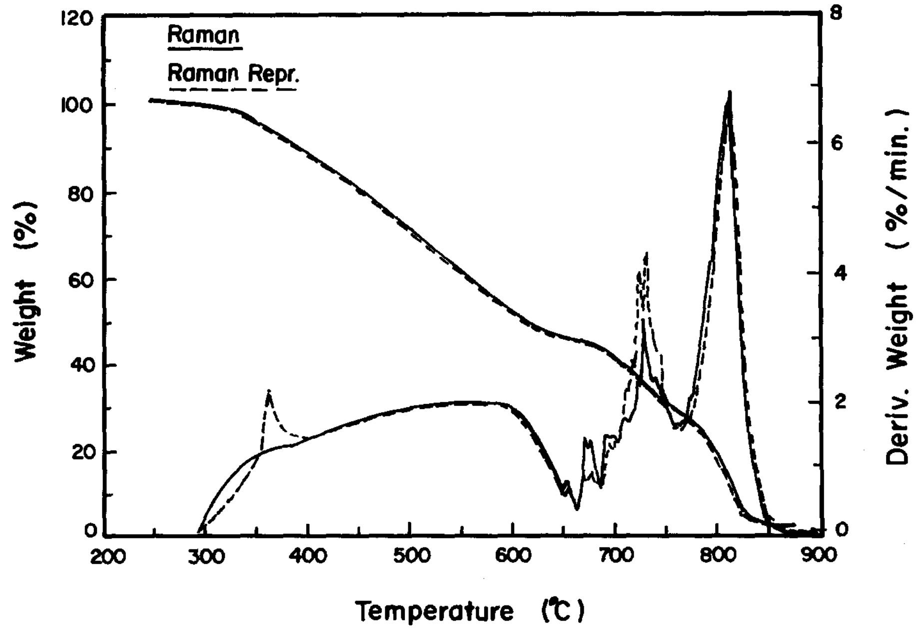

Fig. 5. TGA thermogram of Raman crude oil (combustion).

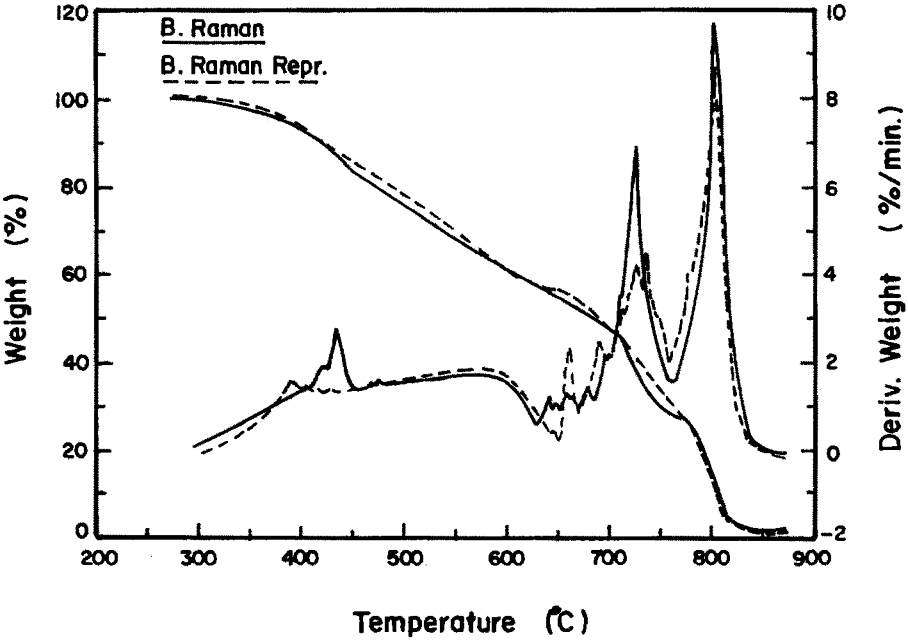

Fig. 6. TGA thermogram of Bati Raman crude oil (combustion).

TABLE 2

Heat properties of crude oils

	Raman	Bati Raman
Peak temp., DSC (K)	812	807
Peak temp., TGA (K)	804	801
Heat flow rate (W g^{-1})	10.8	15.1
Heat evolved, LTO (J g^{-1})	144	89.3
Heat evolved, HTO (J g^{-1})	2490	3602
Total heat (J g^{-1})	2634	3691.3

Kinetic analysis

Kinetic data were obtained from the HTO region of the DSC thermograms, assuming a first order combustion reaction for the fuel laid down in this region. The resulting equation is

$$dh/dt = kh = A \exp(-E/RT)\,h$$

or

$$\log(dh/dt\ 1/h) = \log A - E/2.303RT$$

where h is the fraction of the enthalpy yet to be released and k is the rate constant expressed in terms of the usual Arrhenius relation.

TABLE 3

Kinetic parameters from DSC/TGA curves (HTO)

DSC curves	Raman I	Raman II	B. Raman I	B. Raman II
n (dim.)	1	1	1	1
E (kJ mol^{-1})	128.3	131.6	142.3	147.6
A (min^{-1})	2.1×10^8	7.6×10^8	1.6×10^9	3.3×10^9
TGA curves	**Raman I**	**Raman II**	**B. Raman I**	**B. Raman II**
n (dim.)	1	1	1	1
E (kJ mol^{-1})	146	124	288	276
A (min^{-1})	2.7×10^9	0.3×10^8	2.7×10^{18}	0.7×10^{18}

For analyzing the TGA/DTGA data, the model assumes that the rate of weight loss of the total sample is dependent only on the rate constant, the weight of the sample remaining and the temperature with assumed unity reaction order

$$\mathrm{d}w/\mathrm{d}t = kw = A\exp(-E/RT)\,w$$

or

$$\log(\mathrm{d}w/\mathrm{d}t\ 1/w) = \log A - E/2.303RT$$

where w is the weight of sample remaining and k is the rate constant.

In the HTO region, higher activation energies were found as the API gravity of the crude oil decreased. The high activation energy values for

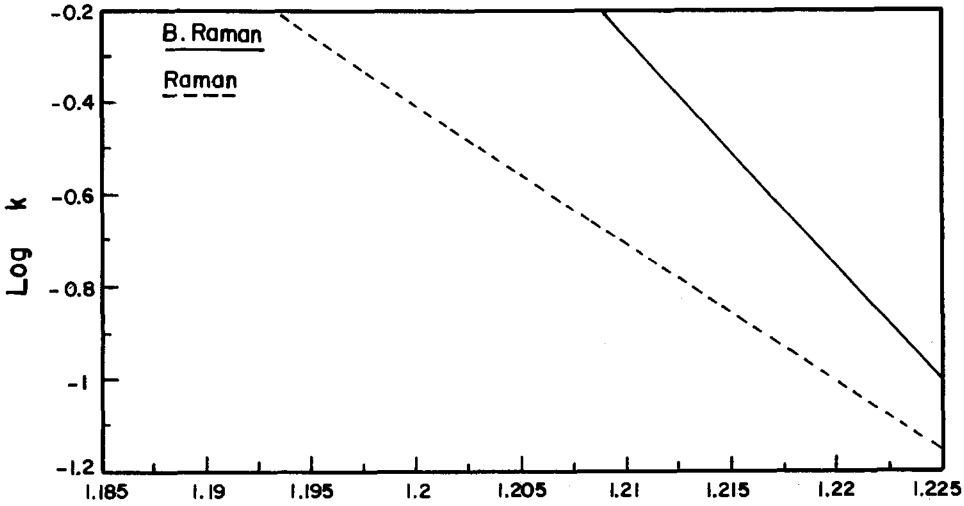

Fig. 7. Arrhenius plot of crude oils (DSC curves).

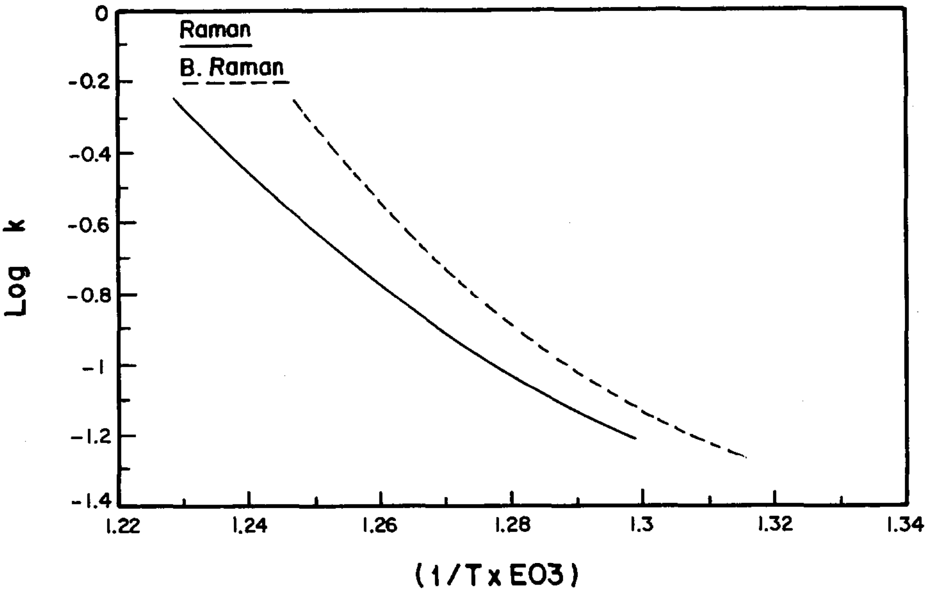

Fig. 8. Arrhenius plot of crude oils (TGA curves).

the high temperature oxidation reactions are due to the high exothermicity of the reactions. The Arrhenius constant A is believed to be a factor dependent on the medium in which reaction is taking place (Table 3). The linear least squares correlation for the identified rectilinear portions varied between 0.95 and 0.99 (Figs. 7 and 8). Similar results were observed for the activation energy and Arrhenius constant values when comparing the reaction parameters of the crude oils by the ratio and the Coats–Redfern methods [7, 8].

CONCLUSIONS

From the experimental study of the DSC/TGA thermograms of Raman and Bati Raman crude oils made in this work, the following chain of conclusions emerges.

(1) In pyrolysis experiments, temperature ranges where distillation and visbreaking occur were identified for the crude oils studied. The heavier oil had deposited larger amounts of residue after distillation was complete.

(2) In the combustion of crude oils with air, three distinct regions were identified, known as low temperature oxidation, fuel deposition and high temperature oxidation.

(3) Higher activation energies were found as the API gravity of crude oils decreased in the HTO region.

(4) Data obtained from the kinetic analysis of the HTO exotherms, assuming a first order reaction, gave values of the activation energy in

good agreement with previously reported values where reaction order was calculated directly from the analysis of the thermograms.

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