EFFECT OF CLAY ON CRUDE OIL COMBUSTION BY THERMAL ANALYSIS TECHNIQUES

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This research was aimed to investigate the role of clay on the combustion and kinetic behavior of crude oils in limestone matrix. For this purpose, simultaneous TG (thermogravimetry) and DTA (differential thermal analysis) experiments were performed at three different heating rates as 10–15 and 20°C min^{-1}, respectively. A uniform trend of decreasing activation energies was observed with the addition of clay. It was concluded that clays surface area affects the values of Arrhenius constant, while it is the catalytic properties of clay, which lower the activation energies of all the reactions, involved in the combustion process.

Keywords: *clay, crude oil, differential thermal analysis, heating rates, reaction kinetics, thermal analysis, thermogravimetry*

Introduction

Crude oil combustion and the factors affecting it play an important role in the application of an in-situ combustion process. The overall transition of crude oil to coke and the eventual combustion of coke are of utmost importance. It is the same characteristic nature of the process that makes thermal analysis techniques highly important research tool. DSC, TG/DTG and DTA techniques have been used as screening tools for in-situ combustion process. Ranjar and Pusch [1] studied the effect of the oil composition, characterized on the basis of light hydrocarbon, resin and asphaltene contents, on the pyrolysis kinetics of the oil and the combustion kinetics of the fuel. The results of their investigations showed that the colloidal composition of oil as well as the transfer-ability and heat transfer characteristics of the pyrolysis medium has a pronounced influenced on fuel formation and composition. Vossoughi [2] has used TG and DSC techniques to study the effect of clay and surface area on the combustion of selected oil samples. The results indicate that there was a significant reduction in the activation energy of the combustion reaction regardless of the chemical composition of additives. Moreover, the low-temperature oxidation of the oil and probably the coke deposition were strongly affected by the specific surface area of the solid matrix. Vossoughi and Bartlett [3] have developed a kinetic model of the in situ combustion process from data obtained from TG and DSC. They used the kinetic model to predict fuel deposition and combustion rate in a combustion tube. Good agreement was obtained between predicted and observed fuel deposition and combustion rate in a combustion tube. Verkocy and Kamal [4] performed TG and pressurized differential scanning calorimetry (PDSC) investigations on Saskatchewan heavy oils collected from wells under primary, steam flood and fire-flood production, and on cores. They have estimated kinetic and thermo-chemical data for thermolysis, low-temperature oxidation and combustion reaction rates, which were non-linearly dependent on the heating, rate. Bousaid and Ramey [5] reported a decrease in activation energy when 20% clay was added to the sand mixture. It was observed that the fuel deposition was much greater for the porous medium with clay content. Fassihi *et al.* [6] performed combustion tube experiments on different crude oils in sand packs containing clay. They observed a significant effect of clay on frontal behavior. Higher fuel deposition found in the presence of clay due to its adsorption characteristics. Rashidi and Bagci [7] investigated the role of clay on thermo-oxidative behavior of crude oil at different pressures. Results indicate that clay content of the matrix influenced the amount of fuel deposited on the limestone. More fuel was deposited as the clay content was increased. They observed a uniform trend of decrease in activation energy by the addition of clay to the limestone. Kök [8] investigated the reaction rates related to an in-situ combustion process were investigated and the effect of heating rate and crude oil type on the reaction rates. Experiments were performed under the same pressure and airflow rate and at two different heating rates. It was observed that oxidation of crude oil porous media follows a series of reactions. These reactions can be divided into three regions: low temperature oxidation, fuel deposition, and high tempera-

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Table 1a Properties of crude oils

Crude oil	^{o}API	Viscosity/cP	Asph./%	C/%	H/%	S/%	N/%
Garzan	26.7	37	12	84.4	11.7	2.8	0.35
Raman	18.7	2260	21	n. a	n. a	n. a	n.a

n. a – not available

ture oxidation. Kisler and Shallcross [9] experimentally studied the oxidation kinetics of a light Australian crude oil using an evolved gas analysis technique. Mixtures of sand, water and crude oil were heated at a controlled rate with a constant how of an oxidizing gas. The effluent gas was continually analysed for its oxygen, carbon monoxide and carbon dioxide contents. The oxidation behaviour was found to be substantially different to that previously observed for heavier crudes. The kinetic parameters for each class of reaction to be estimated. The effects on the kinetic parameters of variables such as pressure, sand grain size and carbon dioxide content of the injection gas were also investigated experimentally. Kök *et al.* [10] determined the combustion characteristics of crude oils in the presence of a limestone matrix using TG/DTG. In combustion with air, three distinct reaction regions were identified in all crude oil/limestone mixtures studied known as low temperature oxidation (LTO), fuel deposition (FD) and high temperature oxidation (HTO). The individual activation energies for each reaction region may be attributed to different reaction mechanisms, but they do not give any indication of the contribution of each region to the overall reactivity of the crude oils. Depending on the characteristics, the mean activation energy of samples varied between 50.3 and 55.8 kJ mol^{-1}. Sonibare *et al.* [11] studied the thermal behavior of the Nigerian oil sand bitumen in an oxidizing environment using non-isothermal TG and DTA. This condition can occur during in situ thermal recovery. The kinetics of the reactions was also determined by Arrhenius plot method. Three regions of mass loss corresponding to low-temperature oxidation, fuel deposition and high temperature oxidation were identified. Increasing the heating rate caused a shift in the reaction regions and peak temperatures to higher temperatures. The exothermicity increased with increasing heating rate. Kök [12] applied simultaneous TG and DTA to light crude oil combustion in the presence and absence of metal oxide. In crude oil-limestone mixture, three main transitional stages are detected. These are distillation, LTO and HTO regions, respectively. In the case of experiments with Fe(III) chloride at different amounts, the shape of TG-DTA curve is changed considerably. Kinetic parameters of the samples are determined using ASTM method. Reduction in activation energy is considered to be an indication of the catalytic activity of the additive.

Table 1b Properties of limestone

Components	Mass%
Calcite	92.0
Dolomite	6.6
Quartz	1.2
Kaolinite	0.2

Experimental

The crude oil samples used during the experiments were from Turkish oil fields. Two crude oil samples (Garzan and Raman) of different properties were mixed with crushed limestone (<60 mesh). The final oil saturation was 15% in the mixture. 5 and 10 mass% of clay was added to the mixture in order to see the effect of clay on combustion. Properties of crude oils and limestone are given in Table 1.

Simultaneous TG-DTA experiments were carried out using Netzsch thermal analysis system. TG has the capability of measuring the mass loss whereas DTA has the capability of measuring the temperature difference either as a function of temperature or time in a varied but controlled atmosphere. Prior to the experiments TG system was calibrated with calcium oxalate monohydrate for temperature readings and silver was used in order to correct for buoyancy effects. Simultaneous TG-DTA experimental procedure involves placing sample (100 mg) setting the heating and gas (air) flow rate, then commencing the experiment. All experiments were performed at three different heating rates (10–15 and 20°C min^{-1}) over the temperature range of 25 to 1200°C. Simultaneous TG-DTA experiments were performed twice for repeatability.

Results and discussion

The role of clay in reservoirs and its possible influence on kinetics of crude oil burning is not entirely clear. However it is known that clay fractions of the reservoir matrix possess the highest surface area and clay fractions are the most chemically reactive of the inorganic constituents present in the reservoir and finally possess catalytic properties toward various organic liquids. The naturally occurring clay minerals mostly consist of silica

and alumina. Clays, silica, alumina and synthetic silica/alumina are classified as solid acid catalysts. Their catalytic activities are related to their acid site density and acid strength. Further, a relationship exists between their acidity and activation energy. Literature on catalytic cracking process [13, 14] reveals that increased catalyst site density and acid strength favor increased rate of coke formation. This, although detrimental to the catalytic cracking process, may be beneficial to the in-situ combustion process in view of greater fuel deposition, especially when light crude oil reservoirs are involved. Theoretically combustion of oil can be initiated whenever oxygen comes in contact with fuel. However, the temperature, composition of the fuel and the oxygen supply dictate the nature of this reaction.

In the course of this research, TG-DTA curves were produced for two different crude oil-limestone mixtures and in the presence of 5–10 mass% of clay. A composite plot of TG-DTA curves of the sample transition obtained in an oxidizing environment is given in Figs 1–3, respectively. In this plots, four stages of transition are observed. These stages are: (i) distillation, (ii) low temperature oxidation, (iii) fuel deposition and (iv) combustion/cracking reactions. These main transitional stages are observed in all of the samples studied, although to different extents. These are the same stages identified in [13]. It was also observed that the heating rate employed in TG-DTA analysis significantly affects fuel lay down, peak and burn-out temperatures. The effect of high heating rate was to cause the reactions to occur at higher temperatures, where probably overlapping and incomplete reactions caused the TG-DTA curves to change. Temperature intervals and peak temperatures
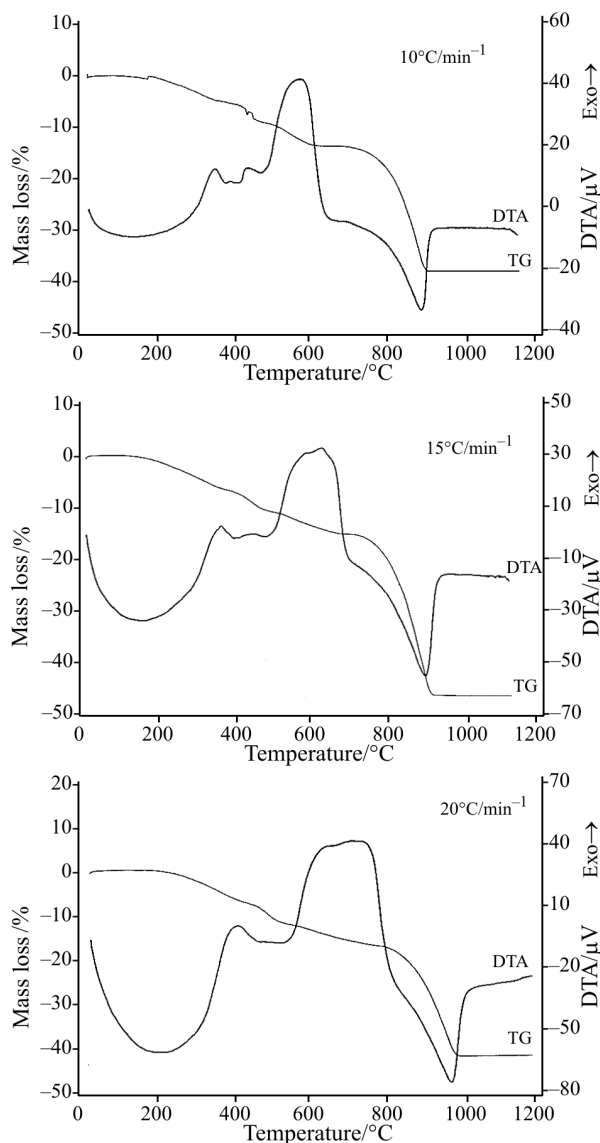
Fig. 1 TG-DTA curves of Raman+limestone at different heating rates
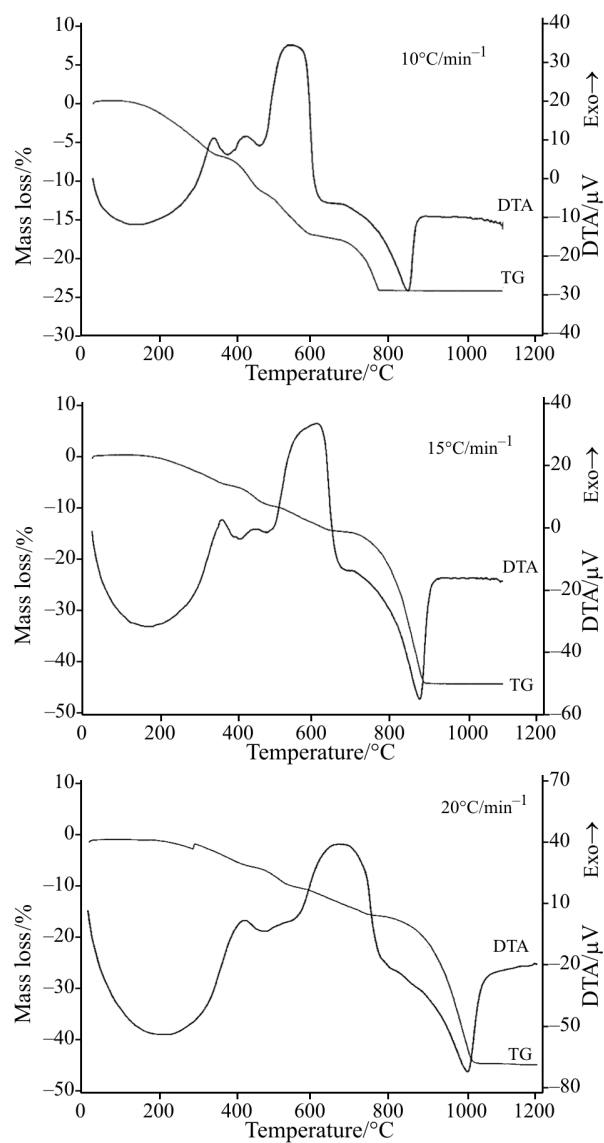
Fig. 2 TG-DTA curves of Raman+limestone+5 mass% clay at different heating rates

Table 2a Reaction intervals and peak temperatures (Garzan+limestone)

Heating rate/ °C min⁻¹	LTO/ °C	Peak temp./°C LTO region	Fuel deposition/ °C	Comb. cracking/ °C	Peak temp. of Comb. cracking/°C
10	300–400	370	400–475	475–645	555
15	300–420	385	420–500	500–680	585
20	300–450	400	450–515	515–730	615

LTO: low temperature oxidation

Table 2b Reaction intervals and peak temperatures (Garzan+limestone+5 mass% clay)

Heating rate/ °C min⁻¹	LTO/ °C	Peak temp./°C LTO region	Fuel deposition/ °C	Comb. cracking/ °C	Peak temp. of Comb. cracking/°C
10	300–400	375	400–480	480–655	560
15	300–435	390	435–505	505–700	590
20	300–455	405	455–520	520–725	620

Table 2c Reaction intervals and peak temperatures (Garzan+limestone+10 mass% clay)

Heating rate/ °C min⁻¹	LTO/ °C	Peak temp./°C LTO region	Fuel deposition/ °C	Comb. cracking/ °C	Peak temp. of Comb. cracking/°C
10	300–400	378	400–490	480–655	565
15	300–440	395	435–510	510–705	595
20	300–460	408	460–530	525–730	630

Table 3a Reaction intervals and peak temperatures (Raman+limestone)

Heating rate/ °C min⁻¹	LTO/ °C	Peak temp./°C LTO region	Fuel deposition/ °C	Comb. cracking/ °C	Peak temp. of Comb. cracking/°C
10	300–390	365	390–475	475–690	588
15	300–420	382	420–505	505–720	615
20	300–430	396	430–510	510–730	635

Table 3b Reaction intervals and peak temperatures (Raman+limestone+5 mass% clay)

Heating rate/ °C min⁻¹	LTO/ °C	Peak temp./°C LTO region	Fuel deposition/ °C	Comb. cracking/ °C	Peak temp. of Comb. cracking/°C
10	300–410	372	410–490	490–695	593
15	300–425	388	425–510	510–735	620
20	300–435	398	435–520	520–750	645

Table 3c Reaction intervals and peak temperatures (Raman+limestone+10 mass% clay)

Heating rate/ °C min⁻¹	LTO/ °C	Peak temp./°C LTO region	Fuel deposition/ °C	Comb. cracking/ °C	Peak temp. of Comb. cracking/°C
10	300–415	375	415–500	500–700	597
15	300–435	390	435–515	515–740	625
20	300–445	400	445–525	525–760	660

of the samples are given in Tables 2 and 3. It was observed that the addition of clay to porous matrix causes more fuel deposition and an increase in combustion peak temperature that suggest that at higher temperatures and in the presence of clay, a stable combustion is possible in a larger range of conditions.

The addition of clays to the porous matrix significantly affects fuel deposition and combustion/cracking regions.

In general, metallic additives and clays present in the sand exert a catalytic influence on the reaction. Therefore, the presence of clay in matrix can influ-

Table 4a Kinetic parameters of the Garzan crude oil in porous matrix

Sample	Activation energy LTO/kJ mol^{-1}	Arrhenius const. LTO/min^{-1}	Activation energy Comb./kJ mol^{-1}	Arrhenius const. Comb./min^{-1}
Garzan+limestone	76.2	3.55·10^5	58.9	5.56·10^2
Garzan+lst+5 mass% clay	74.5	2.29·10^5	56.7	3.72·10^2
Garzan+lst+10 mass% clay	72.0	1.79·10^5	54.2	2.40·10^2

Table 4b Kinetic parameters of the Raman crude oil in porous matrix

Sample	Activation energy LTO/kJ mol^{-1}	Arrhenius const. LTO/min^{-1}	Activation energy Comb./kJ mol^{-1}	Arrhenius const. Comb./min^{-1}
Raman+limestone	87.3	3.37·10^6	82.8	1.41·10^4
Raman+lst+5 mass% clay	85.0	1.84·10^6	75.6	4.53·10^3
Raman+lst+10 mass% clay	80.1	6.81·10^5	69.4	1.70·10^3
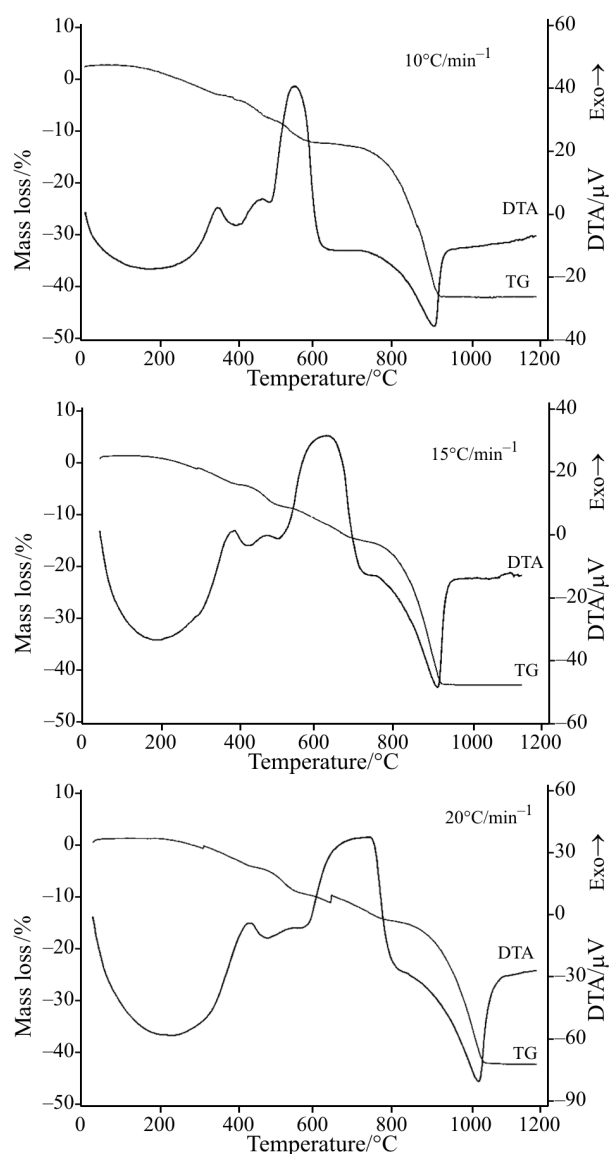
Fig. 3 TG-DTA curves of Raman+limestone+10 mass% clay at different heating rates

ence the kinetic parameters as well as over all in-situ combustion parameters [15]. Non-isothermal kinetic study of combustion process is extremely complex for crude oils in the presence of limestone matrix and clay, because of the presence of numerous complex components and their parallel and consecutive reactions. A method developed by ASTM committee [16] was used throughout the kinetic analysis. Determination of kinetic parameters using peak temperatures requires very precise measurement of reaction peak temperatures for each reaction interval studied as a function of linear programmed heating rates. Throughout the study, it was observed those activation energies and the Arrhenius constants of the reactions (low temperature oxidation and combustion/cracking) involved in combustion process decreased by increasing clay content in the porous matrix, which is the indicative of catalytic properties of clay (Table 4). Reduction in activation energy resulting from the addition of the clay content is observed regardless of the chemical composition of the additive [17–19]. This confirms the catalytic activities of solid additives on combustion. It is also evident that the addition of clay to the limestone matrix causes more fuel deposition and an increase in the combustion peak temperature, which suggests that in presence of clay, a stable combustion is possible in a larger range of conditions.

Conclusions

In this research, simultaneous TG-DTA experiments were carried out to identify the effect of clay on crude oil combustion. The results showed that:

- Activation energies and Arrhenius constants of the samples are decreased by incrasing the caly content in the matrix, indicating the catalytic effect of clay.
- The addition of clay to the limestone matrix caused more fuel deposition and an increase in the com-

bustion peak temperature, which is attributed to catalytic and large specific surface area of clay.

Acknowledgements

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