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EFFECT OF METAL OXIDE ON LIGHT OIL COMBUSTION
TA and kinetic analysis

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Abstract

Simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) were applied 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, low-temperature oxidation (LTO) and high temperature oxidation (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.

Keywords: combustion, crude oil, kinetics and activation energy, metallic additive, thermal analysis

Introduction

The application significance of this research lies in an enhanced oil recovery (EOR) process called in-situ combustion. The application of in-situ combustion process to light crude oil reservoirs is limited by the amount of fuel available for combustion. To artificially regulate the fuel formation and combustion reactions, metallic salts are usually considered as the catalyst because they are water soluble and cheap. The presence of catalyst furnishes additional pathways that allow the reaction to occur more rapidly. It also accelerates oxidation indirectly by destroying the antioxidants that are naturally present in most crude oils.

Burger and Sahuquet [1] 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. Three successive oxidation regions were observed in the DTA curves, namely low-temperature partial oxidation, combustion of crude oil fractions and finally, coke combustion. Drici and Vossoughi [2, 3] applied DSC and TG to crude oil combustion in the presence and absence of metal oxides. Vanadium, nickel and ferric oxides behaved similarly in enhancing the endothermic reactions. In the presence of a large surface area such as on silica, the surface reactions are predominant and unaffected by the small amount of metal oxide present.

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Kinetic analysis of the DSC curves revealed that the activation energies and the frequency factors of the hydrocarbon and the coke combustion reactions, estimated for all metal oxide additives including silica and alumina, followed the same normal compensation trend. Kisler and Shallcross [4] performed experiments to study the effects of various metallic salts on the oxidation kinetics of light crude oil. The experimental results showed that a plot of oxygen consumed *vs.* temperature contained from two to five peaks depending on the salt present. This range of behaviour is substantially different from that observed for heavy oils. The crude oil oxidation reactions were classified into three broad groups depending on the ratio of carbon oxides produced to oxygen consumed. Sodium, copper and iron enhanced the fuel combustion reactions while lithium, magnesium and cobalt reduced the amount of fuel available. Kök [5, 6] used DSC and TG/DTG to characterise the combustion properties of crude oils. In combustion with air, three different reaction regions were identified. DSC and TG/DTG curves have also been used to determine the heat values and the reaction parameters of crude oil samples studied. Kök and Iscan [7] applied DSC to crude oil combustion in the presence and absence of metal chlorides. It was observed that in the presence of smaller ratios of metallic additives, the surface reactions were predominant and the catalyst did not affect the reactions much. Three reaction regions were identified as low temperature oxidation (LTO), middle temperature oxidation (MTO) and high temperature oxidation (HTO). Kinetic parameters of the reaction regions were determined with two different methods and the results are discussed.

The aim of this paper is to discuss the light crude oil combustion in the presence and absence of metal oxide (Fe(III)chloride) in limestone environment using simultaneous TG and DTA systems. The experimental equipment, procedure and data analysis technique are explained next. This is followed by a discussion of the experimental results and conclusions that can be drawn from the research.

Experimental

Simultaneous TG-DTA experiments were carried out using Netzsch thermal analysis system. Prior to experiments, TG-DTA system was calibrated for temperature readings using indium as reference standard. Aqueous solutions of $FeCl_3$ were prepared in concentrations 1, 2, 5, 10 and 15 mol% using distilled water. The crude oil sample was from Beykan (31.5°API) region, whereas a limestone sample used in this research had a particle size of 60 mesh. A typical mixture weighted 100 mg and contained 15 mass% crude oil and 10 mass% $FeCl_3$ solutions. A sample of 100 mg mixture was then transferred to TG-DTA pan and air purge of 50 mL min^{-1} was applied. All the experiments were performed at atmospheric pressure and at three different heating rates (10, 15 and 20°C min^{-1}) over the temperature range of 25–1200°C. All the runs were performed twice for repeatability and totally 32 experiments were performed throughout the research.

Results and discussion

The generally accepted theory of in-situ combustion is that three competing oxidation reactions exist, known as low (LTO), medium (MTO) and high temperature oxidation (HTO). These three classes involve quite different chemical reactions but occur

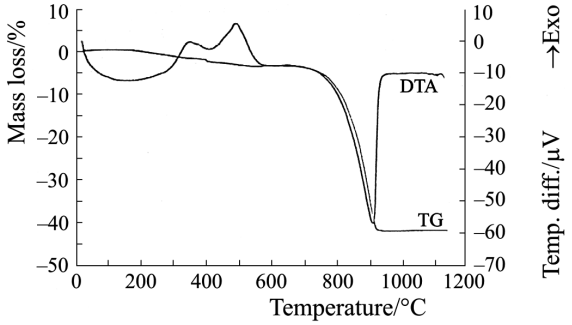

Fig. 1 TG-DTA curves of crude oil–limestone. Heating rate: 10°C min^{-1}

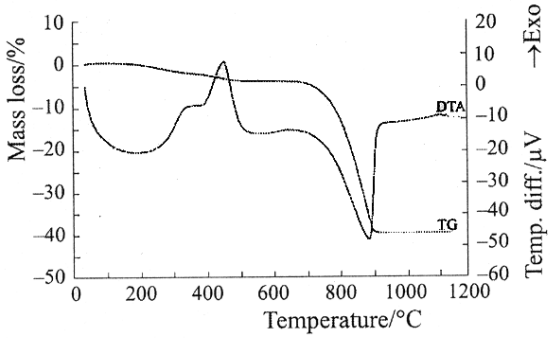

Fig. 2 TG-DTA curves of crude oil–limestone–1% $FeCl_3$. Heating rate: 10°C min^{-1}

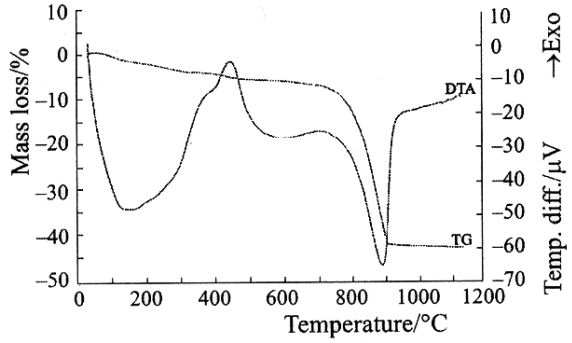

Fig. 3 TG-DTA curves of crude oil–limestone–15% $FeCl_3$. Heating rate: 10°C min^{-1}

across overlapping temperature ranges. Because of the chemical complexity of crude oil, lumped groups of reactions are considered rather than individual reactions (Figures 1–3). In crude oil–limestone mixture, three main transitional stages are detected. These are, distillation between room temperature and about 300°C, LTO between 300–440°C and HTO between 440–640°C respectively (Table 1).

Table 1 Reaction intervals and peak temperatures (crude oil–limestone)

Heating rate/ °C min^{-1}	Distillation region/°C	Low-temperature oxidation		High-temperature oxidation	
		region/°C	peak temp./°C	region/°C	peak temp./°C
10	25–300	300–420	354	420–605	500
15	25–300	300–425	368	425–620	518
20	25–300	300–440	380	440–640	534

In the case of experiments with $FeCl_3$ at different concentrations, the shape of TG-DTA curve is changed considerably. Table 2 compares TG-DTA curves of crude oil combustion in the presence of $FeCl_3$ with increasing amounts of solid additive. As the amount of $FeCl_3$ increased in crude oil mixture, the amount of oil burned during the high temperature oxidation peak on the DTA curve increased. At about 5 mol% content in the mixture, the high temperature oxidation peak started to merge into the low temperature oxidation peak. It is believed that the hydrocarbons that were preferably undergoing cracking in the liquid phase are now being burned on the increasingly available solid surface [3]. As expected $FeCl_3$ caused a significant shift of the exothermic heat released from high temperature oxidation to a lower temperature oxidation region. It was also observed that the heating rate employed in TG-DTA analysis significantly affects fuel lay down, peak and burn-out temperatures. Burn-out temperature represents the temperature where the reaction is completed. 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 for samples studied (Tables 1, 2).

Kinetic analysis

Non-isothermal kinetic study of combustion process is extremely complex for fossil fuels because of the presence of numerous complex components and their parallel and consecutive reactions. A method developed by ASTM committee [8] for chemical reactions provides a means for determining activation energies (E) and Arrhenius constant (A_r) using peak temperatures. 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 that the activation energy values of the crude oil+limestone sample is 81.8 kJ mol^{-1} in low temperature oxidation and 94.7 kJ mol^{-1} in high temperature oxidation regions, respectively. It was also observed that the activation

Table 2 Reaction intervals and peak temperatures of the samples at different Fe(III)chloride concentrations

Heating rate/°C	Reaction region/°C	Peak temp./°C	Burn-out temp./°C
	Crude oil–limestone–1 mol% $FeCl_3$		
10	375–560	455	560
15	405–615	485	615
20	410–630	500	630
	Crude oil–limestone–2 mol% $FeCl_3$		
10	370–560	430	560
15	410–595	480	595
20	420–600	495	600
	Crude oil–limestone–5 mol% $FeCl_3$		
10	400–600	425	600
15	420–610	460	610
20	430–620	470	620
	Crude oil–limestone–10 mol% $FeCl_3$		
10	405–610	420	610
15	425–620	450	620
20	430–625	465	625
	Crude oil–limestone–15 mol% $FeCl_3$		
10	410–610	415	610
15	430–620	445	620
20	440–630	460	630

energies of the samples in the presence of $FeCl_3$ with increasing amounts of solid additive were low than that of crude oil–limestone mixture. Reduction in activation energy and Arrhenius constant is usually considered to be an indication of the catalytic activity of the additive (Table 3).

Table 3 Kinetic parameters of the samples

Sample	Activation energy/kJ mol^{-1}	Arrhenius constant/min^{-1}
Crude oil–limestone	94.7	$4.81 \cdot 10^5$
Crude oil–limestone–1 mol% $FeCl_3$	59.8	$2.40 \cdot 10^3$
Crude oil–limestone–2 mol% $FeCl_3$	53.5	$8.75 \cdot 10^2$
Crude oil–limestone–5 mol% $FeCl_3$	51.8	$8.55 \cdot 10^2$
Crude oil–limestone–10 mol% $FeCl_3$	50.6	$8.15 \cdot 10^2$
Crude oil–imestone–15 mol% $FeCl_3$	49.8	$7.95 \cdot 10^2$

Conclusions

In this research, the combustion kinetics of light crude oil in the presence and absence of metallic catalyst were investigated. It was observed that in the presence of metallic catalyst at different concentrations the combustion behaviour and the kinetics are different from those in the absence of a catalyst. It was found that the catalyst enhanced the fuel combustion reaction in which could be used to stimulate combustion process in the field applications.

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