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CATALYTIC EFFECTS OF METALLIC ADDITIVES ON THE COMBUSTION PROPERTIES OF CRUDE OILS BY THERMAL ANALYSIS TECHNIQUES

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Abstract

Differential scanning calorimetry (DSC) was applied 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.

Keywords: combustion, differential scanning calorimeter, metal oxides and kinetics

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 vaporisation, and minimising 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 a steam. It may also be generated in situ by burning part of the oil in underground reservoirs, a process known as 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. This fuel is produced by oxidation reactions occurring down stream of the combustion front. If less fuel is deposited, the process will not be self-sustaining. By contrast, heavy crude oils can produce too much fuel, which results in either slow advance of combustion front or incomplete combustion of fuel.

Vossoughi *et al.* [1] demonstrated the effect of the sand-grain size on the in situ combustion process through a series of experimental in situ combustion tube runs. They observed that a large portion of the initial oil content was displaced ahead of the front, and insufficient oil was left behind to be coked and consumed as a fuel. However, the oil content ahead of the front was even larger than the initial oil content of the sand pack for the runs involving fine sand grains. Drici and Vossoughi [2] applied

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a thermal analysis technique to the combustion of crude oil in the presence of silica and alumina with a wide range of specific surface areas. They observed a reduction of activation energy for mixtures with a high ratio of surface area to crude oil. Kisler and Shallcross [3] 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. Drici and Vossoughi [4] applied differential scanning calorimetry (DSC) and thermogravimetry (TG/DTG) to crude oil combustion in the presence and absence of metal oxides. It was found that the effect of titanium oxide was similar to that of silica and alumina. Vanadium, nickel and ferric oxides behaved similarly in enhancing the endothermic reactions. 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. They concluded that if the natural logarithm of frequency factor *vs.* all the activation energies of the combusted samples display a straight line with a positive slope, it is called compensation effect. However, this is an indicator of the catalysed phenomenon. 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, known as low temperature oxidation, fuel deposition and high temperature oxidation. DSC and TG/DTG curves have also been used to determine the heat values and the reaction parameters of crude oils.

Experimental

Experiments were performed using a DuPont 9900 thermal analysis system with DSC module. Prior to experiments, the DSC system was calibrated for temperature readings using indium as reference standard. The crude oils used in this research were from Beykan and Karakus crude oil fields. Three solutions of metallic chlorides as $FeCl_3$, $MgCl_2{\cdot}6H_2O$ and $CuCl_2$ were used to prepare crude-limestone and metallic additive mixtures (1 and 2 mole%). Mixtures of oil and solid particles were prepared in a small plastic weighing boat and mixed thoroughly. The experimental procedure involves placing a sample in a pan, setting the heating and flow rate then commencing the experiments. The DSC curves were obtained using the following experimental conditions: atmosphere: air; flow rate: 50 ml min^{-1}; sample mass: 10 mg; heating rate: 10°C min^{-1}. temperature range: 20–600°C. All the experiments were performed twice for reproducibility. Properties of the crude oil samples and the metallic additives are given in Table 1.

Table 1 Properties of crude oils and formula of metallic additives

Crude oil	°API gravity, °API	Viscosity, C_p/20°C
Beykan	31.5	11.7
Karakus	30.1	3.6

Metallic additive	Formula
Ferric chloride	$FeCl_3$
Magnesium chloride	$MgCl_2 \cdot 6H_2O$
Cupric chloride	$CuCl_2$

Results and discussion

Although crude oils are complex mixtures with widely varying physical properties, they undergo similar reactions when heated. In an oxidative environment, three distinct reaction regions were identified in all crude oils studied (Fig. 1). A reaction up to 300°C was actually the first reaction, called low temperature oxidation (LTO). A second transition zone taking place between 300–420°C is called middle temperature oxidation (MTO). The final reaction of the crude oil inferred from the DSC curves takes place between 420–570°C and is called high temperature oxidation (HTO). These three reaction regions involve quite different chemical reactions but occur across overlapping temperature ranges. Low temperature oxidation reactions involve the oxygenation of hydrocarbons. These are heterogeneous reactions between gas and liquid phases. Significant amounts of oxygen are consumed by low temperature oxidation reactions. As the crude oil is heated through intermediate temperatures, it undergoes distillation and pyrolysis. It leads to the deposition of a solid fuel on the reservoir grains and the production of light hydrocarbons in the gas phase. The oxidation

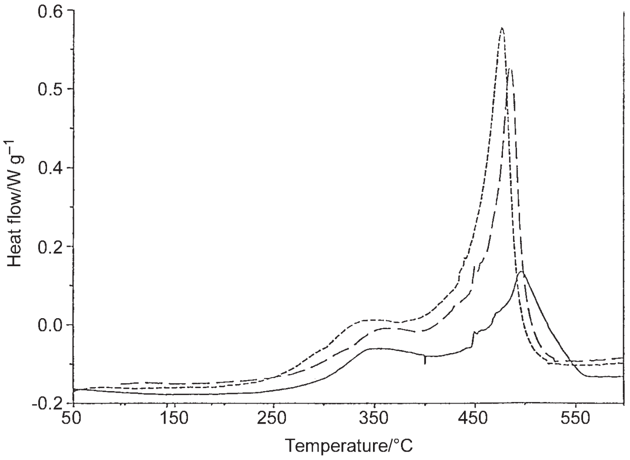

Fig. 1 DSC curves of the samples additives (beykan+limestone+$FeCl_3$)

of these light hydrocarbons is known as middle temperature oxidation. The exothermic high temperature oxidation reactions are heterogeneous (gas–solid) and produce carbon oxides and water. Reaction intervals of the samples are given in Table 2. Low temperature region intervals are found to be very wide in the absence of metallic additives. The presence of these additives decreased the width in these regions. This fact is also true for the middle temperature and high temperature regions. The only exception is the sample of Beykan with 2 mole% of $MgCl_2 \cdot 6H_2O$ in the high temperature region. Peak temperatures increased with the existence of catalysts in MTO regions and they decreased in HTO regions (Table 3). Among the peak temperatures given in Table 3, in $FeCl_3$ with 2 mole% in HTO, a slight increase is seen with the increase of the mole percentage with Beykan crude oil. In Karakus crude oil, the decrease of the peak temperature is observed which is due to the higher viscosity of the oil sample.

Table 2 Reaction intervals of the samples/°C

Sample	LTO	MTO	HTO
Beykan+Limestone	20–290	290–420	420–560
Bey.+Lst+1% $CuCl_2$	20–285	285–420	420–500
Bey.+Lst+2% $CuCl_2$	20–270	270–400	350–480
Bey.+Lst+1% $MgCl_2 \cdot 6H_2O$	20–290	295–400	400–520
Bey.+Lst+2% $MgCl_2 \cdot 6H_2O$	20–275	300–390	390–570
Bey.+Lst+1% $FeCl_3$	20–285	290–370	370–520
Bey.+Lst+2% $FeCl_3$	20–275	290–360	380–520
Karakus+Limestone	20–300	300–400	400–560
Kar.+Lst+1% $CuCl_2$	20–250	250–370	370–520
Kar.+Lst+2% $CuCl_2$	20–230	250–375	360–520
Kar.+Lst+1% $MgCl_2 \cdot 6H_2O$	20–300	300–370	370–510
Kar.+Lst+2% $MgCl_2 \cdot 6H_2O$	20–300	300–400	400–480
Kar.+Lst+1% $FeCl_3$	20–290	290–350	390–510
Kar.+Lst+2% $FeCl_3$	20–250	260–300	380–480

Kinetic analysis

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. Numerous chemical reactions coupled with simultaneous heat, mass and momentum transfer make in situ combustion one of the most difficult enhanced oil recovery methods. In this study, two different kinetic models (Roger–Morris and Arrhenius) were used to analyse the DSC curves.

Table 3 Peak temperatures of the samples/°C

Sample	Peak 1, MTO	Peak 2, HTO
Beykan+Limestone	340	490
Bey.+Lst+1% $CuCl_2$	400	460
Bey.+Lst+2% $CuCl_2$	410	400
Bey.+Lst+1% $MgCl_2·6H_2O$	360	480
Bey.+Lst+2% $MgCl_2·6H_2O$	360	470
Bey.+Lst+1% $FeCl_3$	335	480
Bey.+Lst+2% $FeCl_3$	365	490
Karakus+Limestone	360	490
Kar.+Lst+1% $CuCl_2$	350	440
Kar.+Lst+2% $CuCl_2$	350	440
Kar.+Lst+1% $MgCl_2·6H_2O$	370	400
Kar.+Lst+2% $MgCl_2·6H_2O$	370	390
Kar.+Lst+1% $FeCl_3$	360	460
Kar.+Lst+2% $FeCl_3$	370	450

A kinetic model developed by Roger and Morris gives means of estimation of activation energies from DSC curves. The recorded DSC data are in the form of distances between the curve and the baseline at the specified absolute temperature. This distance is proportional to the rate constant. The activation energy can be calculated from the following expression:

$$-E=R[(\ln D_1-\ln D_2)/(1/T_1-1/T_2)] \tag{1}$$

where, D_1 and D_2 are two distances from the baseline at the associated temperature T_1 and T_2. R is the gas constant (J g^{-1} mole^{-1} K^{-1}) and E is the activation energy (kJ mole^{-1}).

In Arrhenius method, the measured rate of energy loss accounts for the gross changes in the system. Arrhenius type reaction model considers that the rate of energy loss of the total sample is dependent on the rate constant, fraction of the enthalpy yet to be released and the temperature. Therefore, the final form of the equation is as follows:

$$\log[(\mathrm{d}h/\mathrm{d}t)(1/\mathrm{h})]=\log A-E/2.303RT \tag{2}$$

where, h is the fraction of the enthalpy yet to released (mW) and A is the frequency factor (1 min^{-1}).

In this research, experimental data indicate that the grain size distribution is more effective when the additive percentage is low. But the additive becomes more and more dominant as the percentage increases. In the literature it is implied that [2, 4] those in thermal analysis techniques the ratio of the surface area to crude oil displays an inverse proportion with the activation energy. This property is good for in situ applications but, on the other hand, this high ratio increases the amount of residual oil in the front which is not desired. The presence of a catalyst furnishes additional pathways that allow the reactions to occur more rapidly, which means catalysts provide a mechanism with a lower activation energy (Tables 4 and 5). The shifting of the Arrhenius plot to the right with the increase of catalyst percentage indicates the reaction has been positively catalysed (Fig. 2). The same trend has been observed in all the samples studied. The reduction in activation energy is usually considered to be an indication of the catalytic activity of the additive. A reaction can be positively catalysed with an increase in frequency factor even if the activation energy is increased. Therefore, the combined effect of the frequency factor and activation energy must be considered. For a chemical reaction over a series of related catalysts, the following relation is assumed [7].

$$\log A=mE+C \tag{3}$$

where, m and C are constants.

Table 4 Kinetic parameters of the samples (Roger–Morris model)

Sample	E_a/kJ mole^{-1}, MTO	E_a/kJ mole^{-1}, HTO
Beykan+Limestone	86.1	91.6
Bey.+Lst+1% $CuCl_2$	52.8	73.6
Bey.+Lst+2% $CuCl_2$	100.1	105.9
Bey.+Lst+1% $MgCl_2\cdot 6H_2O$	48.9	193.8
Bey.+Lst+2% $MgCl_2\cdot 6H_2O$	32.7	85.2
Bey.+Lst+1% $FeCl_3$	48.1	140.5
Bey.+Lst+2% $FeCl_3$	28.8	149.9
Karakus+Limestone	59.7	69.7
Kar.+Lst+1% $CuCl_2$	170.5	175.7
Kar.+Lst+2% $CuCl_2$	72.8	86.3
Kar.+Lst+1% $MgCl_2\cdot 6H_2O$	100.1	129.7
Kar.+Lst+2% $MgCl_2\cdot 6H_2O$	74.7	87.3
Kar.+Lst+1% $FeCl_3$	68.2	71.7
Kar.+Lst+2% $FeCl_3$	62.9	80.2

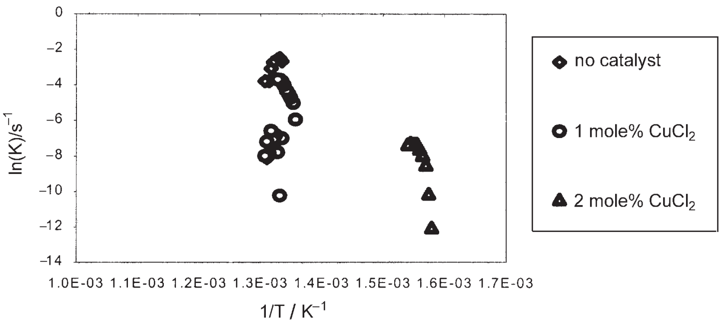

Fig. 2 Kinetic plot in the existence and absence of metallic additives (beykan+limestone+$CuCl_2$)

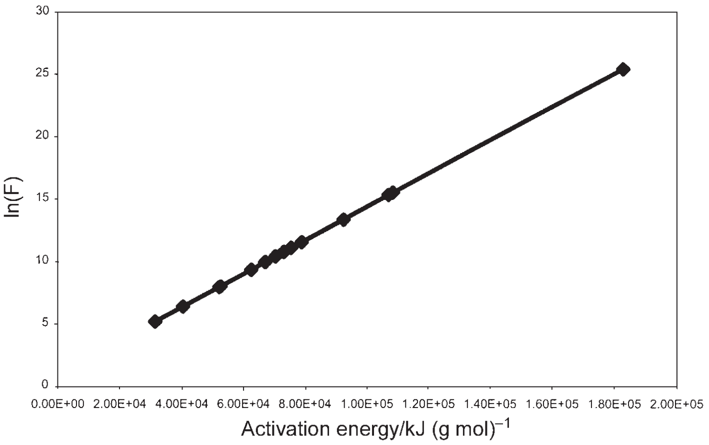

Fig. 3 Compensation effect of the combustion in the presence of metallic additives

Table 5 Kinetic parameters of the samples (Arrhenius model)

Sample	E_a/kJ mole^{-1}, MTO	A/ 1/min, MTO	E_a/kJ mole^{-1}, HTO	A/ 1/min, HTO
Beykan+Limestone	92.4	6.50E+05	98.4	5.15E+05
Bey.+Lst+1% $CuCl_2$	67.1	2.15E+04	80.4	6.70E+04
Bey.+Lst+2% $CuCl_2$	107.1	4.60E+06	111.4	2.25E+06
Bey.+Lst+1% $MgCl_2{\cdot}6H_2O$	52.5	3.10E+03	205.8	9.95E+10
Bey.+Lst+2% $MgCl_2{\cdot}6H_2O$	40.3	6.05E+02	92.1	2.50E+05
Bey.+Lst+1% $FeCl_3$	52.1	2.90E+03	152.2	2.30E+08
Bey.+Lst+2% $FeCl_3$	31.4	1.80E+02	165.3	1.00E+09
Karakus+Limestone	62.4	1.15E+04	77.8	5.05E+04
Kar.+Lst+1% $CuCl_2$	84.6	1.15E+11	182.2	6.90E+09
Kar.+Lst+2% $CuCl_2$	75.4	6.65E+04	91.3	2.30E+05
Kar.+Lst+1% $MgCl_2{\cdot}6H_2O$	108.4	5.55E+06	138.8	5.00E+07
Kar.+Lst+2% $MgCl_2{\cdot}6H_2O$	78.8	1.05E+05	94.2	3.20E+05
Kar.+Lst+1% $FeCl_3$	73.1	4.80E+04	76.3	4.20E+04
Kar.+Lst+2% $FeCl_3$	70.3	3.40E+04	88.2	1.65E+05

This is usually called the compensation effect and m is related to the temperature at which all the rates become equal, T_s. It can also be shown that;

$$m=(2.303RT_s)^{-1} \tag{4}$$

The linear fitting and the positive slope of log$A$ *vs.* activation energy both for middle and high temperature oxidation reactions indicate overview of positive catalysation.

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