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KINETICS OF LIQUID HYDROCARBON COMBUSTION USING THE DSC TECHNIQUE

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ABSTRACT

TGA/DSC techniques were applied to the combustion of crude oil in the presence of solid particles of various specific surface areas. The major physical and chemical transitions observed were classified into three groups, namely distillation, liquid hydrocarbon combustion and coke combustion. This paper deals with the peak associated with the liquid hydrocarbon combustion.

Kinetic study revealed that the liquid hydrocarbon combustion peak consisted of two types of combustion reactions which could not be modelled with a single power-law-type kinetic model. Oxygen concentration of the purging gas was varied and its effect on the DSC curve was monitored. It was noticed that at low oxygen concentration, i.e. in the range of 5 to 10%, two distinct peaks emerged. Kinetic analysis of each peak produced a power-law kinetic model for each reaction. The kinetic model was first-order with respect to oxygen partial pressure for both peaks. The order of reaction with respect to the hydrocarbon content was unity for the first peak and 1.5 for the second peak. Optimization of all the data produced a reaction order with respect to the surface area of -0.57 for the first peak and -0.2 for the second peak.

INTRODUCTION

Crude oil combustion has been studied by various investigators. The methods of investigation are widely different. Recently, the potential of thermal analysis techniques has been realized. It seems that thermal analysis techniques have advantages over other methods of investigation, being simpler to run and more readily amenable to kinetic analysis. Tadema [1] applied differential thermal analysis (DTA) to crude oil combustion in 1959 and recognized two distinct exothermic reactions from the DTA curves. Other investigators [2–4] applied DTA to study the influence of porous media on crude oil combustion. Bae [5] applied both DTA and thermogravimetric analysis (TGA) techniques in studying the effect of certain variables on fire flooding. Recent works [6–14] have made use of TGA curves combined with differential thermogravimetric (DTG) curves and differential

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scanning calorimetry (DSC) in kinetic studies and have revealed the distinct physical and chemical transitions involved when a sample of crude oil experiences a constant heating rate with air purge, in the presence or absence of reservoir rock. This work is an extension of our earlier work involving further characterization of the overlapping peaks encountered in the DTG curves produced from crude oil combustion in the presence of solid particles.

EXPERIMENTAL

A DuPont 951 Thermogravimetric Analyzer and a 910 Differential Scanning Calorimeter with R90 programmer and a Hewlett-Packard 7046 A *X*–*Y* recorder were used in this study. The crude oil used was from Iola field, Allen County, Kansas, with an API gravity of 19.3 (938.3 kg m^{-3}) and viscosity of 530 cp (0.53 pa.s) at 25 °C. The sample weight for all the TGA runs ranged from 10 to 50 mg and that for DSC runs was kept around 12 mg. Air and purging gas with oxygen concentrations of 5, 10, 40 and 50% were used to produce TGA/DTG and DSC curves for each crude oil/solid particle mixture. The heating rate was kept constant at 10 °C min^{-1} for all runs.

CHARACTERIZATION OF THERMOGRAMS

Figure 1 presents a typical TGA/DTG curve generated for the crude oil in the presence of solid particles undergoing a constant heating rate with air

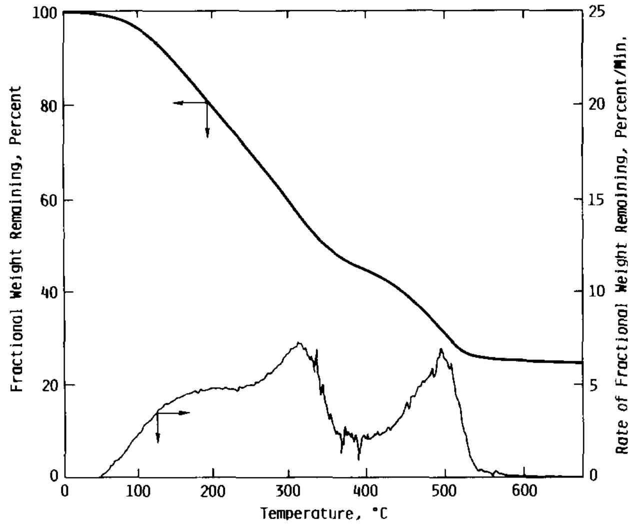

Fig. 1. Typical TGA/DTG curves of Iola crude oil in the presence of silica particles and air purge.

purge. The DTG curve clearly demonstrates three distinct transitional stages, namely distillation, combustion of liquid hydrocarbons and, finally, coke combustion. Analyses of the distillation and coke combustion peaks have already been reported elsewhere [11,12]. This paper is concerned with only one peak, namely the final exothermic peak at the high temperature end of the broad distillation peak. This is the result of the liquid hydrocarbon combustion which was reported earlier [14] as low temperature combustion. It is highly exothermic and can easily be detected on the DSC curve. The influence of the distillation peak on the hydrocarbon combustion peak was removed by carrying out the DSC runs at low sensitivity. This was verified by producing a horizontal base line for a DSC run under the same conditions with nitrogen purge gas.

KINETIC ANALYSIS

Kinetic analysis was performed by assuming a power-law kinetic model with unknown power-law parameters to be determined from experimental DSC curves, i.e.

$$\mathrm{d}H/\mathrm{d}t = KH^n P_{\mathrm{O}_2}^m A^l \tag{1}$$

where $\mathrm{d}H/\mathrm{d}t$ is the rate of heat released with respect to time, H is the enthalpy yet to be released, P_{O_2} is the oxygen partial pressure, A is the specific surface area of the solid particles, K is the specific rate constant, and n, m and l are the reaction orders with respect to H, oxygen partial pressure and specific surface area respectively. It is understood that H, the enthalpy yet to be released, is directly proportional to the hydrocarbon oil content in the mixture. The specific rate constant, K, was assumed to follow the Arrhenius equation for temperature dependency

$$K = F_{\mathrm{f}} \exp(-E/RT) \tag{2}$$

where F_{f} is the frequency factor, E is the activation energy, R is the universal gas constant and T is the absolute temperature. Kinetic analysis involved determination of the effect of hydrocarbon content, oxygen partial pressure and specific surface area of the solid particles on the reaction rate. In doing so, one variable was changed while the other two were kept constant. Kinetic analysis revealed that the DSC peak could not be adequately described with one power-law kinetic model. Therefore, it was suspected that more than one type of reaction was involved in this peak. In an attempt to, possibly, separate these two reactions, the oxygen partial pressure was varied in the range 50–5%. As shown in Figs. 2 and 3, lowering the oxygen partial pressure resulted in a separation of the two reactions. Kinetic analysis of the DSC curves was performed for both reactions assuming a reaction order of unity with respect to the specific surface area

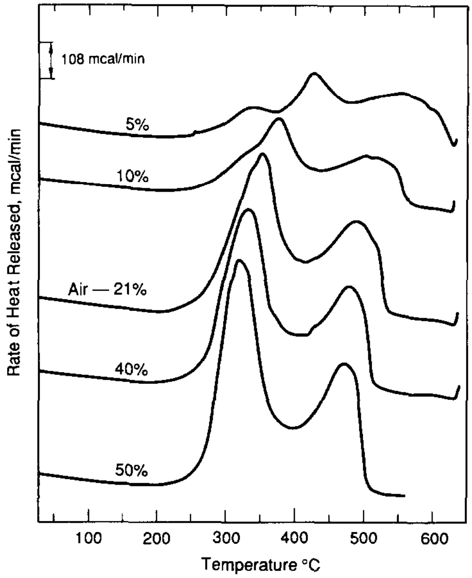

Fig. 2. DSC curves of Iola crude oil/alumina particles #2 in purging gas of different oxygen partial pressure.

of the granular materials ($l = 1$). The corresponding Arrhenius plots are presented in Figs. 4 and 5 for the first and second reaction respectively. It is evident that the assumption $l = 1$ is not valid. To determine a more accurate value for l, both optimization as well as trial and error techniques were

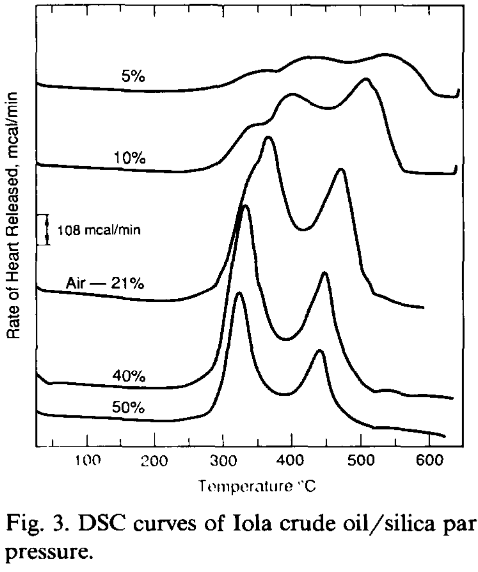

Fig. 3. DSC curves of Iola crude oil/silica particles in purging gas of different oxygen partial pressure.

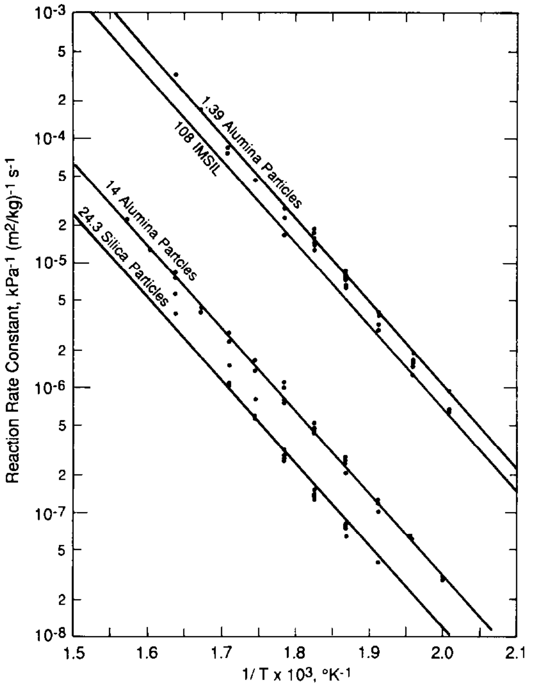

Fig. 4. Arrhenius plot for DSC peak #1 assuming $l=1$.

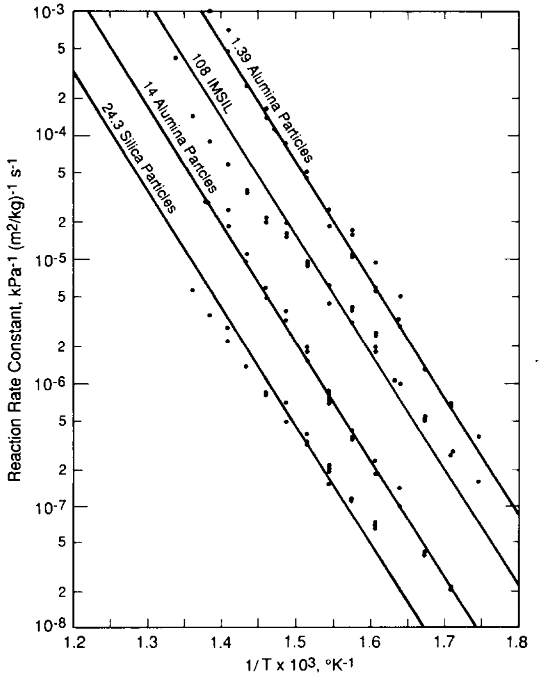

Fig. 5. Arrhenius plot for DSC peak #2 assuming $l=1$.

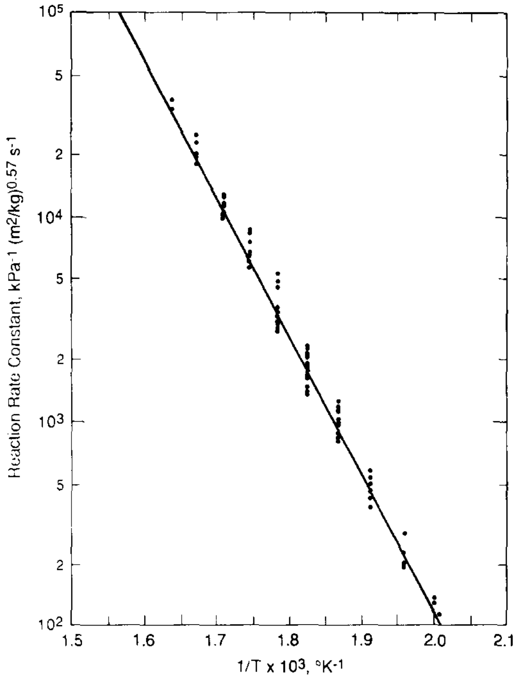

Fig. 6. Arrhenius plot for DSC peak #1 assuming $l = -0.57$.

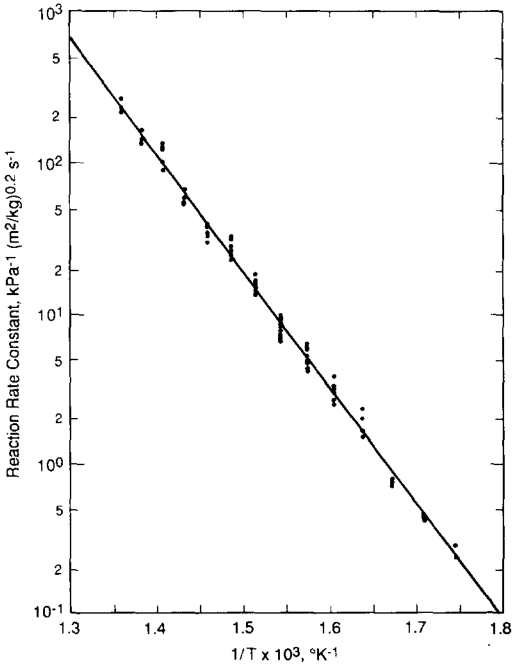

Fig. 7. Arrhenius plot for DSC peak #2 assuming $l = -0.2$.

applied. The best fit for the data of the first peak corresponded to $l = -0.57$, and $l = -0.2$ for the second peak. Therefore the kinetic model produced for the first reaction associated with the liquid hydrocarbon combustion peak is given by

$$\mathrm{d}H/\mathrm{d}t = KP_{O_2}HA^{-0.57} \tag{3}$$

and for the second reaction by

$$\mathrm{d}H/\mathrm{d}t = KP_{O_2}H^{1.5}A^{-0.2} \tag{4}$$

The Arrhenius plots generated from the entire data set are presented in Figs. 6 and 7 for the first and second reaction respectively. The specific rate constants produced from the best straight-line fit through the data presented in Figs. 6 and 7 are $K = 2.02 \times 10^5 \exp(-139.3/RT)$ for the first reaction and $K = 200 \exp(-145.2/RT)$ for the second reaction.

DISCUSSION OF THE RESULTS

The kinetic models generated from the above analysis suggest that the reaction rate depends on the specific surface area to a negative power. That is, the reaction between 290 and 400 °C (554–752 °F) is retarded as surface area is increased. Evidence in the literature [10,15–17] indicates that the fuel laydown increases with increasing surface area. An interpretation of this would be that the surface area retards the burning of the liquid hydrocarbon which will be consumed in a later stage (last peak) as fuel. To further substantiate this hypothesis, the fraction of crude oil burned in the last peak was calculated using the TGA curves. It was noticed that the fraction of the initial oil content consumed as fuel in the last peak increased from 18.6% in the presence of coarse sand (low specific surface area) to 26% in the presence of fine silica particles (high specific surface area).

CONCLUSIONS

From the results presented, the following conclusions can be made.

1. DSC curves are better suited for the kinetic study of the peak under consideration where the main peak is due to distillation. This is particularly appropriate when the exothermicity of the peak due to the liquid hydrocarbon combustion is significantly higher than the main peak.
2. Lowering the oxygen partial pressure of the purging gas successfully separated the two overlapping reactions associated with the liquid hydrocarbon peak.
3. The kinetic models produced for the liquid hydrocarbon combustion reactions reflected a negative reaction order with respect to the specific surface area.

4. The reaction rate constant followed the Arrhenius equation for temperature dependency in both reactions.

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