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TGA/DSC TECHNIQUES AS RESEARCH TOOLS FOR THE STUDY OF THE IN-SITU COMBUSTION PROCESS

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ABSTRACT

This paper summarizes the recent past and the present research activities and predicts the foreseeable future augmentation in the area of TGA/DSC application in the in-situ combustion process. The types of information obtainable from TGA and DSC curves of crude oil combustion can be summarized as: (a) the major crude oil transitions involved, (b) the effect of clay, (c) the effect of the sand grain specific surface area, (d) kinetic data, and (e) combustion feasibility. Presently, research in our thermal recovery laboratory is directed toward a simultaneous run of the thermogravimetric analyzer and the in-situ combustion tube system. This is achieved by bypassing the TGA controller and controlling the TGA oven by the same minicomputer which is monitoring the tube. Therefore, the temperature of the TGA oven will be brought close to the temperature of a point in the tube from which the gas sampling probe will direct the flowing gas to the TGA sample pan. It is anticipated that TGA curves obtained in this fashion will reveal the actual physical and chemical transitions occurring in the tube and provide some insight into the mechanisms involved. In view of the results published recently, it is concluded that quantitative prediction of the combustion tube test behavior using TGA/DSC technique is possible.

INTRODUCTION

Although TGA/DSC techniques have been widely used as research tools in different areas, such as the polymer, food, and even coal industries, their application in research related to the petroleum industry has been limited. Finger-printing of crude oil is one area in the petroleum industry where differential thermal analysis (DTA) has been extensively used. Recent advancement in equipment design of the thermal analysis techniques and the need for deeper understanding of the detailed mechanisms involved in some of the enhanced oil recovery (EOR) processes might play a significant role in bringing these two disciplines closer together. One of the promising EOR processes for the application of the thermal analysis techniques is the in-situ combustion process. In-situ combustion, commonly known as fire-flooding, is a thermal recovery method mostly suitable for medium to heavy crude oil

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reservoirs. In this process a small portion of the crude oil is burned in situ to displace the remaining oil. The process is very complex in comparison with other recovery techniques. It involves miscible and immiscible displacement mechanisms such as gas, steam, water, and light hydrocarbon displacement. In addition, crude oil undergoes physical and chemical changes which must be understood and quantified before any reliable prediction of the process performance can be expected. It is this latter requirement which makes the thermal analysis methods viable research techniques for the process. Although DTA and in some cases thermogravimetric analysis (TGA) have been used in the past for studying crude oil combustion, the studies were limited to qualitative approaches. It has been only in recent years that the extended potential of the thermal analysis techniques has been recognized. This paper summarizes the recent past and the present research activities in this area and predicts the foreseeable future advancement.

APPLICATION OF THERMAL ANALYSIS TECHNIQUES

Tadema [1] seems to be the first investigator who applied DTA to crude oil combustion in his study of the in-situ combustion process. He recognized two distinct exothermic reactions from DTA curves of crude oil combustion in the presence of sand in a dynamic air purge. Burger and Sahuquet [2] used DTA to illustrate the effect of metal oxides and how the properties of both oil and porous media influence crude oil combustion. The effect of reservoir rock, especially its clay content, on crude oil combustion was also depicted by other investigators [3,4] using the DTA technique. Bae [5] applied both DTA and TGA techniques to 15 crude oils ranging from 6 to 38° API gravity. He classified them into three groups based on their thermal analysis curves. He concluded that DTA and TGA techniques were useful tools in studying the effect of certain variables in fire-flooding and only qualitative prediction was possible. Recent works [6–8], however, indicate that quantitative prediction of the combustion tube test behavior is also possible.

The types of information obtainable from the TGA and differential scanning calorimetry (DSC) curves of crude oil combustion are (a) the major crude oil transitions involved, (b) the effect of clay, (c) the effect of the sand grain specific surface area, (d) kinetic data, and (e) combustion feasibility. A brief description of each type of information is given in the following paragraphs.

Major crude oil transitions

Crude oil is a complex mixture. It undergoes many transitional stages during an in-situ combustion process, such as distillation, thermal and catalytic cracking, pyrolysis, coke deposition and combustion, etc. The ideal would be to know each individual constituent of the crude oil and study its physical and chemical changes during an in-situ combustion process. The combined behavior of the crude oil constituents would determine the overall behavior of the in-situ combustion process. This, of course, is an impossible task. Therefore, the idea of dividing the many complicated reactions occurring simultaneously during the combustion of a crude oil into three to four pseudo-component reactions becomes appealing. Pseudo-component reactions are determined from TGA/DSC tests of the crude oil. TGA/DSC tests of the crude oil from a Kansas oil reservoir [6] revealed four major transitional stages: distillation, low temperature oxidation, and first and second combustion/cracking reactions. Each stage of transition was successfully isolated and studied. An empirical kinetic model was produced and applied to the process. Fuel laydown, the time for consumption of the fuel within the combustion zone, and the rate at which fuel was consumed were predicted. Results of the combustion tube runs were in good agreement with predicted values. The prediction technique of the fuel laydown was extended to two more Kansas oil revervoirs. [7]. Close agreement was observed between the fuel deposition predicted by this approach with that obtained experimentally by the in-situ combustion tube runs.

A similar study was later carried out by Jha and Verkoczy [9]. They studied two crude oils from Lloydminster, Canada and observed three groups of chemical reactions occurring in three temperature ranges. In addition, they estimated kinetic parameters for each reaction regime.

Effect of clay

Because of their large surface area, containing many active sites, clays act as a catalyst. The catalytic effect of clay on the in-situ combustion process has been depicted by many investigators [2–4,8,10–14]. Kinetic analysis of the TGA and DSC curves has indicated [8] a significant reduction in activation energy of the coke combustion due to the addition of clay to the crude oil/sand mixture.

Effect of the sand grain specific surface area

TGA and DSC tests were performed [15] on crude oil combustion in the presence of silica and alumina with variable specific surface area ranging from 30 $cm^2\ g^{-1}$ to 24.3 $m^2\ g^{-1}$. Other additives, such as vanadium oxide, titanium oxide, and iron oxide, were also studied [16]. It was noticed that decreasing the crude oil/surface area ratio enhanced the low temperature oxidation peak. Additives with large specific surface area shifted a large portion of the exothermic heat from a higher to a lower temperature range. Further, the effectiveness of the solid additives did not depend only on the availability of the surface area but also on the nature of the surface area. In the case of iron oxide, the endothermic reactions were significantly enhanced.

Kinetic data

Recently, a kinetic study of crude oil combustion was carried out using the TGA technique with the idea of producing a kinetic model capable of reflecting the effect of the specific surface area of the sand grain. The kinetic model produced [17] indicates that the rate of combustion of the coke, $d\alpha/dt$, is proportional to the coke content yet to be burned, α; oxygen partial pressure, P_{O_2}; and specific surface area of the sand grain, S, to the power 0.14; i.e.,

$$\frac{d\alpha}{dt} = k\alpha P_{O_2} S^{0.14} \tag{1}$$

The rate constant, k, follows the Arrhenius equation for temperature dependency

$$k = A \exp(-E/RT) \tag{2}$$

where A is the frequency factor; E, activation energy; T, absolute temperature; and R, gas constant. The above kinetic model was tested for the range of specific surface area from 0.126 to 24.3 $m^2\ g^{-1}$, oil content from 10 to 58 wt% and oxygen partial pressure from 0.05 to 0.5 atm.

Feasibility study

A feasibility study of the in-situ combustion process was carried out for Kansas oil reservoirs [18]. The technique applied was innovative in that the effect of reservoir rock on crude oil combustion was taken into account. This was achieved by performing TGA/DSC experiments on the crude oil/reservoir rock mixtures of the pre-screened Kansas oil reservoirs. The minimum amount of the oil content necessary to sustain the combustion was calculated from these tests. Reservoirs with oil contents above this minimum value were considered suitable for the in-situ combustion process. In-situ combustion tube experiments performed on actual reservoir rocks obtained from Kansas fields confirmed the validity of the prediction.

PRESENT ACTIVITIES

Results summarized above indicate that TGA/DSC techniques are highly viable research tools for studying the in-situ combustion process. However, the techniques have shortcomings. TGA/DSC experiments lack fluid flow phenomena associated with the in-situ combustion process. On the other hand, due to the integral nature of the in-situ combustion tube experiments, any kinetic study of the process from the tube runs seems highly difficult if not impossible. Therefore, combining the two systems and running them simultaneously seems desirable. Presently, research in our thermal recovery laboratory is directed toward a simultaneous run of the thermogravimetric analyzer and the in-situ combustion tube system. Details of the in-situ combustion tube assembly being utilized in this project are discussed elsewhere [10]. Preliminary results indicate that the proposed approach is feasible. The temperature and the composition of the internal environment of the in-situ combustion tube is duplicated in the TGA analyzer which will run simultaneously with the in-situ combustion tube system. This is achieved through by-passing the TGA controller and controlling the TGA oven with the same mini-computer that monitors the tube. Therefore, the temperature of the TGA oven will be brought close to the temperature of a point in the tube from which the gas sampling probe will direct the flowing gas to the TGA sample pan. It is anticipated that TGA curves obtained in this fashion will reveal the actual physical and chemical transitions occurring in the tube and provide some insight into the mechanisms involved.

FUTURE ADVANCEMENT

Incorporation of TGA/DSC results in the mathematical modeling of the in-situ combustion process seems a logical augmentation of the research in the near future. Present approaches [19–21] do not reflect the actual chemical and physical changes occurring in the crude oil in an in-situ combustion process. Therefore, TGA curves produced under the same temperature and gas environment as the in-situ combustion tube experiments seem to be of a more realistic nature. The idea of dividing the many reactions occurring during the combustion of a crude oil into three to four pseudo-component reactions, such as distillation, low temperature oxidation, and combustion/cracking reactions, might prove feasible for crude oils other than those studied so far. It might be possible to divide the many complicated reactions occurring simultaneously during an in-situ combustion process into reactions involving three to four pseudo-components and derive a kinetic model for each pseudo-component reaction. Pseudo-component reactions are detected from the crude oil TGA/DSC curves.

CONCLUSIONS

In view of recently published results it is concluded that TGA/DSC techniques are highly viable research tools for studying the in-situ combustion process. TGA/DSC tests of crude oil combustion provide information on: (a) major crude oil transitions and kinetics of each transition; (b) fuel laydown; (c) rate of fuel consumption; (d) effect of clay and the sand grain specific surface area, and (e) feasibility of the process. Incorporation of TGA/DSC results in the mathematical modeling of the process seems a logical extension of the research in the near future.

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