

THE USE OF THERMAL ANALYSIS TECHNIQUES TO OBTAIN INFORMATION RELEVANT TO THE *IN-SITU* COMBUSTION PROCESS FOR ENHANCED OIL RECOVERY

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The *in-situ* combustion technique of enhanced oil recovery may be used for the recovery of heavy oil deposits. In order to predict when this process may be used computer-based simulators are being developed. The data required by these simulators are currently available from two sources: (i) combustion tubes; these are complex, expensive and time consuming to run; (ii) thermal analysis techniques; these are fast, small-scale and relatively inexpensive. Thermal analysis literature relevant to the process is reviewed and related thermal analysis studies being conducted at Salford University are described.

Keywords: enhanced oil recovery, *in-situ* combustion technique, pressure DSC (1000 psi)

Oil recovery - the *in-situ* combustion process

Exploitation of the reserves of an oil reservoir typically takes place in three stages, termed primary, secondary and tertiary recovery. The first two stages may recover up to 40% of the original oil in place. One of the tertiary techniques used to recover the remaining oil is *in-situ* combustion (ISC). This process involves igniting the formation, the combustion reaction being sustained by the simultaneous injection of an oxidant gas. The mechanism of this process involves converting some of the oil into a 'coke' which is subsequently burned as fuel. The heat evolved from these combustion reactions reduces the viscosity of the oil

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thereby improving its mobility and hence recoverability. This heat can also crack some of the heavier fractions to produce an upgraded oil. Thus the fluid produced by an ISC project offers the potential advantage of oil upgrading over alternative methods of oil recovery.

Before implementing an enhanced oil recovery (EOR) technique an oil company will require evidence of the potential success in terms of the enhanced production available as a result of implementing the procedure. This evidence may be provided by a computer-based simulator. The simulators currently available require information regarding the reservoir and oil characteristics, such as the geology of the formation, the composition of the oil, and the kinetics of the various combustion processes. Since ISC is generally employed as a tertiary method of oil recovery the reservoir characteristics will generally be available. The combustion kinetic information will probably not be available and has to be obtained from laboratory investigations.

Two types of laboratory study are conducted to obtain data for *in-situ* combustion simulators: (i) combustion tubes, and (ii) thermal analysis techniques. Combustion tubes are basically high-pressure tubular reactors (typically 0.1 m dia \times 1 m length). These tubes are filled with reservoir rock (consolidated or ground) and oil. The tube is well instrumented with thermocouples and is run adiabatically using external band heaters. The tube is pressurised to the typical formation pressure and an oxidant gas passed through the tube. The tube contents are ignited at the inlet and the bed is allowed to burn. The temperature profile along the tube is recorded as a function of time, and the exhaust gases and produced oil are analysed. This piece of equipment provides information on the ability of the formation to sustain combustion under a particular set of conditions, on the percentage oil recovery, and on the fluid and heat transfer characteristics of the formation. These experiments are expensive in terms of finance and time. The thermal analysis techniques of TG, DTG and DSC are complementary to the combustion tube. These techniques are used to provide information such as heats of reaction (oxidation and combustion) and reaction rates which may be relevant to the ISC process. These experiments have the advantage over large-scale experiments such as the combustion tube, in that they require small samples (20–50 mg) and, as they are relatively short timescale (1 hr) experiments, a range of conditions can be investigated comparatively quickly. The effect of the surface area of the matrix, catalysts and other additives and oil composition are some of the factors which are investigated using these methods. For the experiments to have relevance to the field situation they must be conducted at pressures equivalent to those experienced by the formation and for this reason high-pressure TG and DSC equipment (1000 psi) should be used.

This paper presents a review of the literature available on the use of thermal analysis techniques to evaluate parameters pertinent to the ISC process and will

demonstrate their relevance. Further, the results of work conducted at Salford University will be reviewed particularly with respect to light oil combustion which is directly relevant to the future exploitation of North Sea reserves.

Review of previous thermal analysis studies

Oil deposits vary in nature from porous rock blocks impregnated with oil of varying viscosity and density several hundred feet underground to sand deposits, the sand grains being coated in a high-density highly viscous tar which may outcrop at the surface and thus be suitable for open-cast mining.

In-situ combustion may be applied to any of these deposits. The common feature concerning an ISC project being conducted in any of these formations is the complexity of the process. This involves coupled heat and mass transfer, fluid flow, matrix-oil interactions and the numerous chemical reactions which occur on thermal treatment of the oil. It is in the last two categories that TG and DSC can provide information.

Thermal analysis techniques have been applied to crude oil combustion since the late 1950s [1-3]; however not until recently has the ISC process in particular been targeted and experiments been conducted quantitatively [4, 5]. TG and DSC yield complementary information. TG shows weight losses as a function of time and temperature and thus gives an overall picture of the processes occurring. The situation may be simplified by performing the experiment in a nitrogen atmosphere rather than air, in which case the oxidation reactions are absent. DSC will only show those processes for which there is a distinct energy transfer; thus the oxidation and combustion reactions are easily observed in an air atmosphere but the distillation process which results in a large weight loss in TG is observed only as a minor endotherm. In a nitrogen atmosphere the DSC trace is much simpler, showing only the non-oxidative processes such as distillation.

A typical result is shown in Fig. 1. This result is for a crude oil without any mineral matrix. The important regions of this plot are:

(i) The large weight loss from ambient to 300°C coupled with a very shallow endotherm on the DSC curve. This is distillation of the lighter fractions of the oil.

(ii) The region between 200° and 300°C is considered to involve combustion of liquid hydrocarbons and is responsible for the slightly more rapid weight losses in air than nitrogen. The distillation, combustion and fuel laydown reactions are interrelated in that enhanced cracking, to produce more fuel, simultaneously produces more light liquid hydrocarbons for combustion and decreases the amount of oil which is distilled.

(iii) In the region between 300° and 400°C, low-temperature oxidation of the oil (LTO) occurs in air. In this process the oil is oxidised to produce ketones, al-

dehydes, alcohols and other oxygenated species, and coke is deposited as fuel for the combustion reaction. It is notable that on comparing this region of the curve with the curve obtained in a nitrogen atmosphere, that the sample gains weight indicative of the oxidation reaction.

(iv) At 400°–450°C and 450°–500°C the first and second combustion reactions occur. These reactions are also referred to as high-temperature oxidation (HTO) and involve combustion of the coke deposited during the LTO process. In a nitrogen atmosphere, it can be seen that in the second region (300°C) a less rapid weight loss occurs than in air. This is attributed to the lack of liquid hydrocarbon combustion and enhanced pyrolysis and cracking reactions. The sample in this case does not undergo LTO but a second pyrolysis and cracking step occurs at about 450°C to leave a residue at 600°C.

Thus it can be seen that the ISC process involves competing reactions – i.e. distillation *vs.* fuel deposition, pyrolysis *vs.* combustion – and it is the extent to which these reactions occur that governs the success or failure of the project. In an idealised situation an inert atmosphere would exist just forward of the combustion zone (due to complete consumption of the oxygen in the oxidant gas stream by the combustion reaction) and so the fuel deposition process could be reproduced in TG experiments using a nitrogen atmosphere. This, however, is an idealised situation and in reality there will be some oxygen present ahead of the combustion front due to channelling and inefficient combustion. The presence of this oxygen will complicate the fuel deposition process. An examination of the fuel laydown process is therefore usually made in the presence of oxygen, and the effect of its partial pressure on fuel laydown [7] and combustion [8–10] are determined. Since the reactions occurring during the ISC process are believed to be at least partly heterogeneous (e.g. coke combustion is gas/solid) an examination has been made of the nature of the matrix on which the oil is deposited and its effect on the process. Vossoughi *et al.* [10] found that the presence of ‘surface area’ (mineral matrix) altered the shape of the DTG curve (Fig. 1), enhancing the liquid hydrocarbon combustion peak at 300°C and causing the two combustion peaks to merge (Fig. 2). This behaviour is obviously closer to the process occurring in the real oil formation than is that depicted in Fig. 1. It is proposed that the presence of the mineral matrix results in more fuel deposition and hence the simultaneous production of more light hydrocarbons which are subsequently combusted. The effects of the mineral matrix on the various reactions involved in the ISC process have been described. In the distillation region [11], the initial rise of the DTG curve was found to be zero order with respect to hydrocarbon concentration but 0.14 with respect to surface area. At higher temperatures distillation was found to be first order in hydrocarbon concentration. The liquid hydrocarbon combustion region [8] was found to consist of two processes, both of which had negative orders with respect to surface area. This type of behaviour implies a retardation ef-

fect as the surface area is increased. It was proposed that an enhancement of the competing fuel laydown reaction, by the increase in surface area, was decreasing the amount of material available for combustion, thus exerting a retarding effect on this process. Coke combustion [10] was found to have an order of 0.14 with respect to surface area as was found for distillation. It was considered that the in-

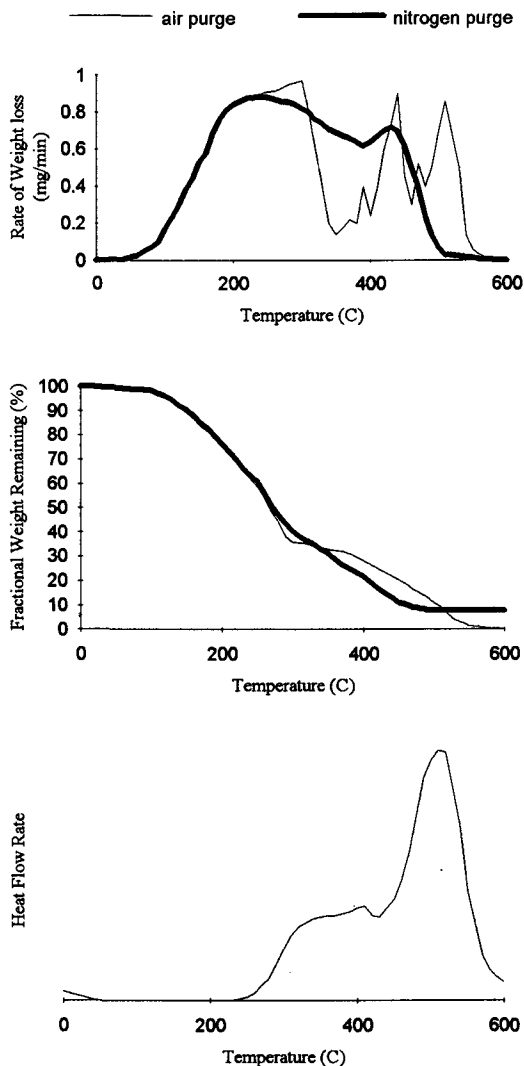


Fig. 1 TG, DTG and DSC curves for a crude oil under air and nitrogen atmospheres [6]. (From Ref. [6], reprinted with permission of the authors and SPE © 1987 Society of Petroleum Engineers)

creased surface area exerts its effect by adsorbing more of the oil and facilitating a greater fuel laydown. Evidence for this mechanism is observed in the form of enhanced LTO peaks on DSC curves [13]. A simultaneous decrease in size of the HTO peaks is often observed. A possible explanation for these observations is that there are two mechanisms for fuel laydown, one which requires oxygen and one which does not. The mechanism which requires oxygen is enhanced by the increase in surface area (and oxygen partial pressure) and produces an oxygenated fuel which results in larger LTO peaks, but which has a lower energy value than the material produced by the other mechanism thus resulting in smaller HTO peaks.

Most of the kinetic investigations have been performed using a power law model and assuming an Arrhenius-type dependence of rate constant on temperature [14]. These models have proved satisfactory, although as pointed out by Nickle *et al.* [7], they should be regarded as a simplistic approximation of the true kinetics. Lin *et al.* [15] proposed an alternative model for tar sand pyrolysis. This model is a modification of the Anthony-Howard [16] distributed activation energy model. In this model there is assumed to be a Gaussian distribution of activation energies, each of which have an Arrhenius-type dependence. This model is more realistic than the power law model since it accounts for more than one reacting species. The model was also proposed for the coke combustion reaction [9].

A reservoir rock frequently contains clays in the host matrix. The effect of these clays has been determined by the addition of kaolinite to sand/oil samples [5] and performing DSC experiments on them. The peak temperatures for the LTO and HTO processes were observed to decrease with addition of clay, thereby inferring a catalytic effect of the clay. Jha and Verkoczy [17] examined the effect of thermal treatment on the clays themselves. The kaolinite was converted to an amorphous intermediate on heating the sample to 600°C. This obviously has implications for the results of experiments in which the effect of clays on the combustion process at this temperature are investigated. The authors also observed that the concentration of fines (particles <2 µm) increased on heating and suggested that this could cause problems by blocking the reservoir pores during the implementation of this process in the field.

Recent work has sought to investigate the combustion process at a more fundamental level. Jha and Verkoczy [18, 19] investigated the effect of thermal treatment on the individual SARA (saturates, aromatics, resins, asphaltenes) fractions of a crude oil. It was observed that the resin and asphaltene fractions had the greatest coke-forming tendencies. The coke formation of a whole crude was accurately predicted from knowledge of the SARA composition of the oil, thereby indicating that the SARA components act independently under thermal stress. The aim of the research detailed in this review has been to provide relevant data with which to model the ISC process. Laboratory TG and DSC experiments are not conducted under field conditions since some of these are difficult to

reproduce (particularly the temperature behaviour). Experiments aim to reproduce combustion tube conditions and the results are then translated for the field situation using well developed correlations. Nickle *et al.* [7] discuss the effect of operating parameters on the results obtained by TG and DSC and their relevance to the field situation. It was noted that experiments should be conducted under the same conditions as apply in the field or the combustion tube since changing some of the parameters will drastically affect the predictions made from the results. This point was emphasised by Vossoughi, who developed a model for predicting the feasibility of combustion in a reservoir [20]. The model operated successfully in many situations, but predicted combustion at a lower specific surface area than was actually achieved in practice [21]. Thus the models developed are not yet complete.

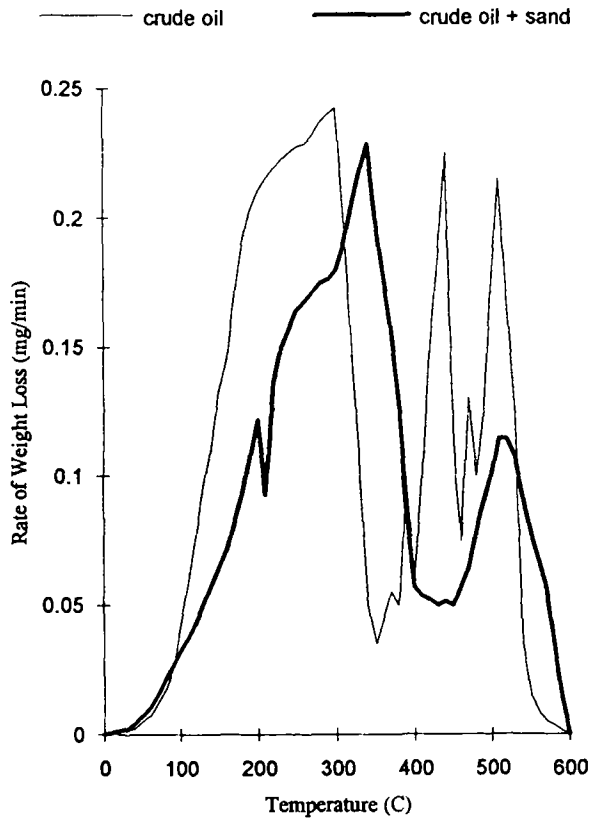


Fig. 2 Effect of surface area on the DTG curve of a crude oil [10]. (From Ref. [10], reprinted with permission of the authors and SPE © 1989 Society of Petroleum Engineers)

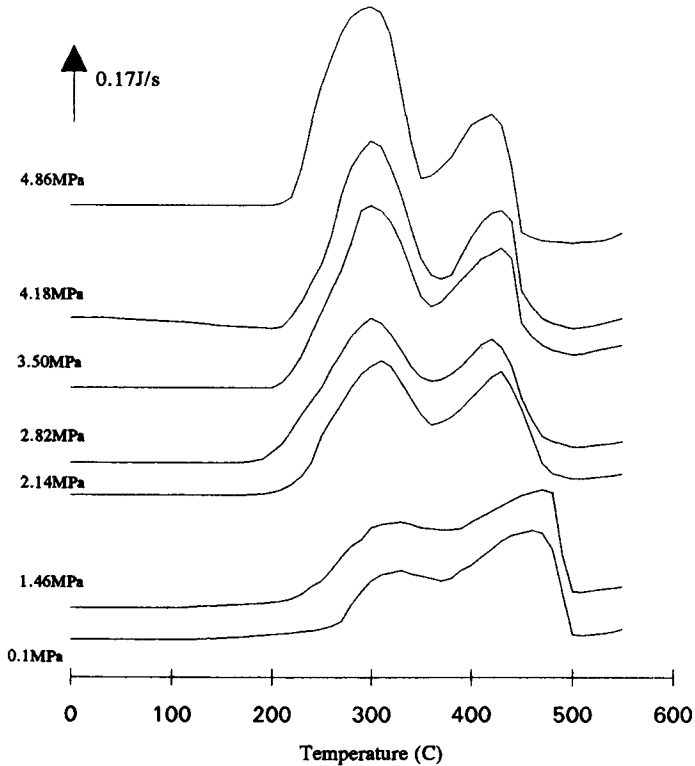


Fig. 3 Pressure DSC curves for a heavy oil/sand mixture, 10/90 wt.%; sand particle size 75 μm

In order to obtain results which will more accurately model the behaviour of the oil in a combustion tube, Vossoughi [14] proposed an experiment where a TG or DSC cell is controlled at the same temperature as a section of a combustion tube during a run. For greater accuracy it is further proposed that the gas from a sampling probe, at the same position in the combustion tube as the thermocouple which is controlling the cell, be passed through the cell during the experiment. Thus the sample would be in the same environment as the material in the combustion tube and its behaviour should be more relevant. While this experiment is useful in theory, it is obviously difficult to conduct in practice.

One of the points raised by Nickle [7] and which has been rarely addressed in the literature is the effect of pressure on the ISC process. Most of the TG and DSC experiments reported have been conducted at atmospheric pressure even though, as reported by Nickle [7] and Phillips [4], pressure can have a substantial effect

on the process. The variation in the results obtained at different pressures could lead to false predictions in translating the information to a field project.

Investigations in the authors' laboratory [22, 23] have been concerned with the thermal treatment of heavy oils using pressurised DSC (PDSC). Experiments were performed at up to 7 MPa (1000 psig) and revealed that high-pressure data cannot be extrapolated from results obtained at low pressure. In general the total heat generated by combustion of a given sample increased with increase in pressure, although the distribution of this increase between LTO and HTO was dependent on the matrix particle size used.

The conclusions of this survey are that data obtained from TG and DSC experiments may be used profitably to simulate the ISC process and also to investigate the reactions occurring. It must be noted, however, that in order to produce representative data the experimental conditions should mimic as near as possible those found in the combustion tube or field situation.

PDSC studies of the ISC process at Salford University

Studies in the authors' laboratory have investigated the effect of surface area, partial pressure of oxygen and oil density, on the heat evolved during the combustion of an oil sample. The effect of total pressure has also been investigated in some detail.

Experimental

Experiments were performed in a Du Pont 910 pressure DSC cell capable of being operated at up to 7 MPa (1000 psig). The cell was controlled by a Du Pont 990 programmer/analyser. Sample size was typically 20 mg. The gas mixtures used were commercially available oxygen : nitrogen mixtures. Experiments have been performed on Marguerite Lake and Wolf Lake heavy oils, Athabasca tar sand and Forties (North Sea) light oil.

Results and discussion

The initial experiments on heavy oil show the marked effect of increased total pressure (Fig.3). It can be clearly seen that an increase in total pressure results in an increase in the total heat evolved by the sample. Further, the effect is more pronounced in this case for the LTO than for the HTO process. Other results show

that this effect is also surface-area-dependent in that a larger particle size causes the HTO peak to increase more than the LTO peak as the total pressure is increased. An increase in the partial pressure of oxygen was shown to result in an increase in the total heat output from the system up to a level of 35%. At concentrations greater than this there was no additional heat release.

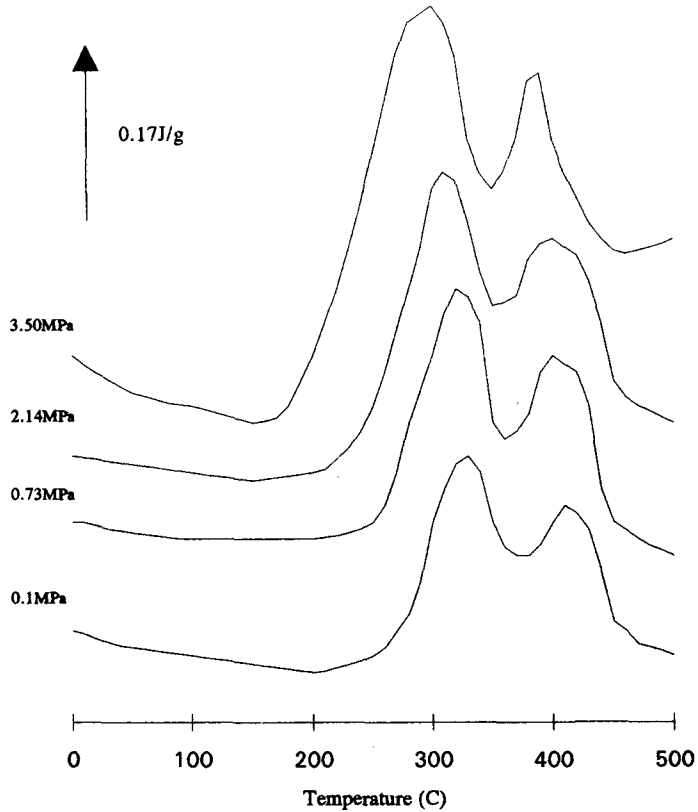


Fig. 4 Pressure DSC curves for a North Sea core

Experiments performed on a light oil (Forties) show an enhancement of the LTO process relative to the HTO process (Fig. 4) as pressure is increased. This is attributed to the lighter nature of the oil which is considered to be more susceptible to the liquid combustion and oxidation reactions which occur in the LTO region of the DSC curve, the increased pressure would tend to prevent evaporation / distillation of the oil and hence more material would be available for reaction. Contrary to the results for a heavy oil, an increase in the specific surface area of the particulate matter was found to enhance the HTO peak (at atmospheric

pressure) for the light oil samples (Fig. 5). An increase in the partial pressure of oxygen was found to increase the total heat evolved and to move the peaks to lower temperatures.

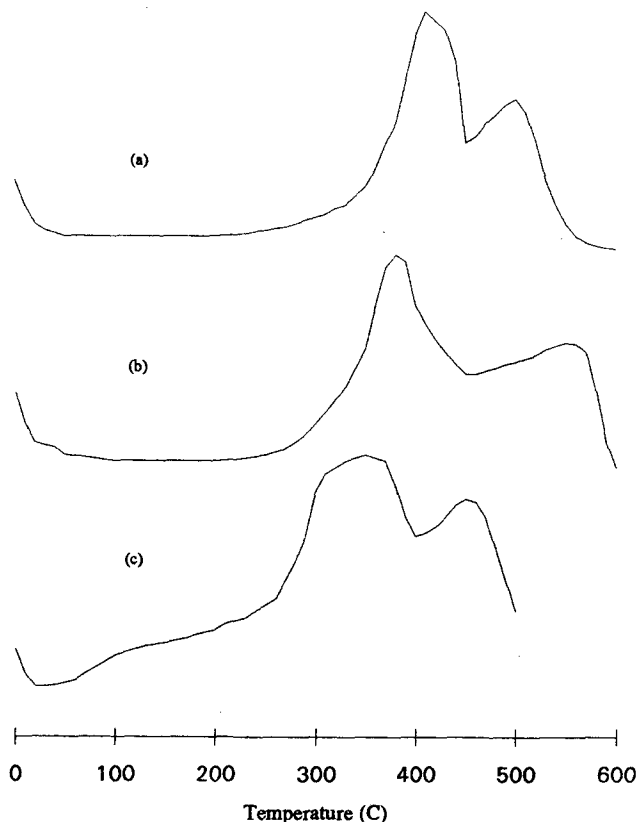


Fig. 5 DSC curves for a North Sea oil at atmospheric pressure in air. a) 297 μm sand, b) 150 μm sand, c) 74 μm sand

The dependence of the effect of partial pressure on heat evolution was investigated at different total pressures by plotting $\delta\Delta H / \delta P_{\text{O}_2}$ (Fig. 6) against total pressure [24]. These plots show that as the total pressure is increased, the effect of an increase in partial pressure of oxygen diminishes until this has no further effect. This is interpreted as evidence of a 'saturation' effect in which after the saturation point the oxygen is reaching all the 'active sites' in the sample at a high enough rate for the heat evolution to be controlled by some other parameter. Presumably before this point the availability of oxygen to the sample is determining the rate of heat evolution. This 'saturation' point was found to occur at a

lower total pressure for larger mineral particles than for small ones. It is assumed that the smaller particles having a greater specific surface area have a higher oxygen 'demand' and so require a higher pressure before the availability of oxygen is sufficient for the reaction to be otherwise controlled. The implication of this result is that if reservoir conditions are such that a high injection pressure is required, then only a low concentration of oxygen is needed and this requirement could be met by compressed air. For a lower-pressure reservoir, however, a higher oxygen concentration may be required to achieve efficient combustion and so oxygen-enriched air may be necessary.

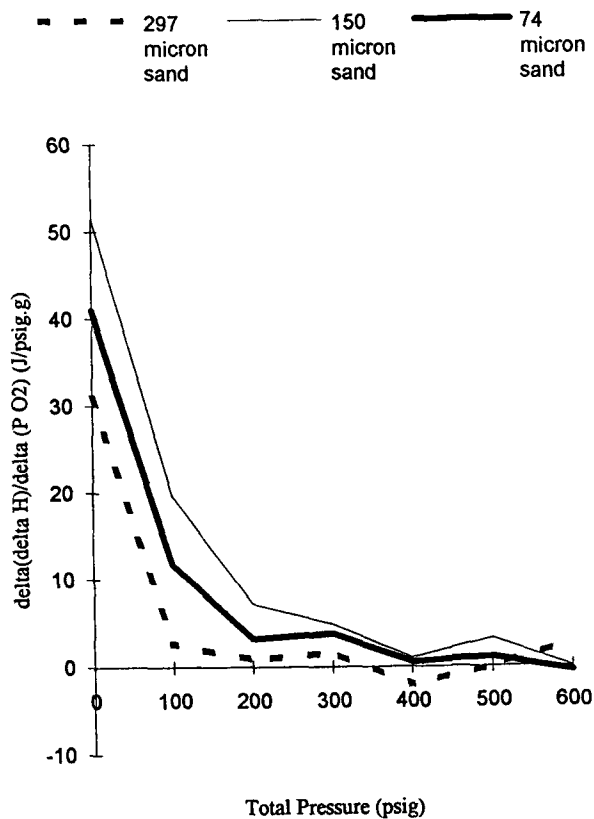


Fig. 6 Effect of partial pressure of oxygen on the heat evolved at different total pressures during the LTO process of a North Sea oil for 75 μm , 150 μm and 297 μm sand

Conclusions

TG and DSC techniques have yielded much useful information regarding the ISC process. The effects of many of the pertinent variables have been investigated and useful predictive models have been established in order to enable the selection of fields suitable for the application of the process. Investigations in the authors' laboratory have revealed the pressure variable to be important when transferring small-scale data (TG, DSC) to the large scale (combustion tube or field). Increased pressure was shown to enhance the amount of heat evolved by a sample although the exact mechanism of this effect depends on the density of the oil. An oxygen saturation effect was observed in some of the experiments at high pressure, which was considered to be evidence of a change in control of the heat evolution reactions away from oxygen-limiting kinetics. These results have relevance where the use of oxygen-enriched air is being contemplated as the oxidant gas for an ISC project.

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The Salford experimental studies discussed in this paper were carried out by Mohamed Belkharouché [23], Surat Indrijarso [22] and Agnes B. A. Lukyaa [24]. The authors thank the SERC and BP Ltd for financial support.

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Zusammenfassung — Die *in-situ*-Verbrennungstechnik der verbesserten Ölrückgewinnung kann zur Rückgewinnung von Schwerölrückständen verwendet werden. Um die Einsatzmöglichkeiten dieses Prozesses zu ergründen, werden computergestützte Simulatoren entwickelt. Die für diese Simulatoren notwendigen Daten können aus zwei Quellen gewonnen werden: (i) Verbrennungsrohre; ihre Anwendung ist kompliziert, teuer und zeitaufwendig; (ii) thermoanalytische Methoden; diese sind schnell, kleingelegt und relativ nicht teuer. Es wird ein kurzer Überblick über die auf diesen Prozeß bezogene Thermoanalysen-Literatur gegeben und es werden verwandte, an der Salford-Universität durchgeführte thermoanalytische Untersuchungen beschrieben.