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Exothermicity Characteristics of Wolf Lake Heavy Oil, Athabasca Tar Sand and Medium Heavy Clair Oil

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Abstract

High pressure accelerating rate calorimetry (ARC) tests have been performed on three different crude oils, at their respective reservoirs pressures. The experiments on medium heavy Clair oil and heavy Wolf Lake oil used clean silica sand, incorporating 3% kaolinite, to represent the reservoir matrix, whereas Athabasca Tar Sand was used in its preserved, virgin state. The Clair oil and Wolf Lake oil tests involved high initial water saturations, representative of either, a post-waterflooded or a post-steam injection state, in the reservoir. A second test on Athabasca Tar Sand used a lower oil (bitumen) saturation, but without adjusting the original brine saturation. Although the medium Clair oil exhibited high exothermicity, throughout the temperature range, the temperature detected for the onset of low temperature oxidation (LTO) was much higher than that for Athabasca Tar Sand. The calculated activation energies also indicate that Athabasca Tar Sand is very reactive in the LTO region. Furthermore, the overall continuity exhibited by the measured exotherms, indicates that all three oils are potentially good candidates for in situ combustion, as an oil recovery method.

Introduction

The most important factor governing the selection, ultimately, of any improved oil recovery (IOR) process, is the availability of a suitable fluid to inject into the reservoir. Even when a fluid agent has been identified for application in a particular reservoir, it needs to be easily deliverable, and available in sufficiently large volumes. Otherwise, the prospect of improved oil recovery is academic. For an increasing number of reservoir situations, air injection is gaining increasing attention for both heavy and light oil recovery. Air injection, into heavy oil reservoirs, otherwise referred to as in situ combustion (ISC), or 'fire flooding', has been applied with varying degrees of success, over the last 40 years. The most recent heavy oil projects are in the Cambay Basin, India (1), using conventional ISC, and the first field pilot at Christina Lake, using the advanced THAI (Toe-to-Heel Air Injection) process (2). There have also been significant developments in high pressure air injection into light oil reservoirs, as evidenced by economically viable air injection projects in the Williston Basin, and project feasibility studies for Barrancas, Argentina

(3), and Cantun, Mexico (4). In the latter case, air injection is seen as a possible replacement for more expensive nitrogen injection. The future IOR prospect in the latter case is huge, some 56 billion barrels of accessible resource.

There are many economic and technical benefits deriving from air injection – excellent displacement efficiency, mobilization of extra oil ahead of the combustion zone, reservoir pressurization, oil swelling from produced CO_2, flue gas stripping, injection gas substitution and, for high pressure, hot reservoirs, and there may be additional factors, such as spontaneous ignition and near miscibility effects.

The accelerating rate calorimeter (ARC) was first advocated as technique for screening oil reservoir candidates for air injection by Yannimaras and Tiffen (5). The technique was developed as a method for studying the reaction kinetics by following reactions adiabatically, especially at high pressure. Moreover, the method can provide insights to explain the occurrence of low temperature oxidation (LTO) and high temperature oxidation (HTO), the two regions where there is significant oxygen uptake. LTO reactions involve direct oxidation of the liquid phase, i.e. oxygen addition reactions, producing aldehydes, ketones, carboxylic acids, alcohols and peroxides, that can, if the residence time for reaction is sufficiently long, decompose finally to water and carbon oxides (6). Degraded, more viscous oil, can also result if the oil composition is susceptible to the formation of more stable, oxidized compounds. However, in the LTO mode, reactions can result in either bond scission or oxygen addition. Moore et al. (7) indicate that the key to success is to design the process for operation in the bond scission mode, which they point out is favoured in many high pressure light oil reservoirs, if the oxygen flux is high enough. The lesson from a large amount of ISC experience, accumulated from technical successes as well a technical failures, especially in heavy oil reservoirs, is to avoid operation in the LTO region. Rather, one should design the process for stable operation in a region where vigorous combustion is obtained, by using a sufficiently high air injection flux, so stable propagation of the combustion front is achieved.

To date, investigations using the ARC technique have focused mainly on light oil applications. In this paper, results are presented for heavy crude oils and also Athabasca Tar Sand, to see if the measures of oxidation reactivity obtained are relevant when considering the application of air injection processes using conventional ISC or THAI.

Experimental

ARC Equipment: the 'PhiTech2' ARC apparatus was supplied by Hazard Equipment Laboratory (HEL) Ltd. The main apparatus consists of a pressure shell, inside which the calorimeter 'bomb', or test cell, is placed (**Fig. 1**). The cylindrical test cell is surrounded by a top guard heater as well as side and bottom guard heaters. The system is fitted with wall thermocouples and a thermocouple is also positioned inside the test cell. These temperature measurements are used to maintain the reaction 'bomb' and its contents in a near-adiabatic condition. The test cell was modified for continuous air flow, by connecting a $1/16^{th}$-inch gas take-off line. There is a larger, $1/8^{th}$-inch line connection on the top of the cell (**Fig. 2**), which is used for air injection. This connection can also be used for charging oil and reservoir material into the test cell. Air is injected into the test cell under mass flow meter control. Gas exits the cell under backpressure control and it is then dried before passing to gas analysers, to measure the concentrations of CO_2, CO and O_2.

Procedure: in order to conduct high temperature–high pressure ARC tests, it is first necessary to carryout a calibration test. After calibration, the ARC test involves a 'Heat-Wait-Search' (HWS) procedure. Heat Loss Calibration (HLC) is necessary to counteract heat loss from the test cell over the range of evolving temperatures. The temperature of the guard heaters was set to be slightly than that of the test cell. The HWS procedure involves heating the test cell and its contents to successively higher temperatures, allowing the cell and its contents to equilibrate at each stage. During the subsequent 'search' period, an automatic procedure determines if the detection limit for an exotherm has been exceeded, i.e. that it has occurred. The guard heaters are then set to the 'tracking' mode to follow the evolving temperature. If not, the entire sequence is repeated by raising the temperature of the test cell by the specified increment.

Preparation of Oil and Rock Sample: the oil and reservoir rock material were used as supplied, using the following procedure:
(i) the test cell was cleaned, dried and weighed.
(ii) unconsolidated reservoir material (75-150 BS mesh) was carefully weighed.
(iii) the volume of oil was measured using a precision syringe.
(iv) oil and reservoir material were loaded separately into the test cell, via the $1/8^{th}$ -inch connection (air injection line).
(v) the reservoir material was 'free flowing' and easily loaded into the cell, followed by the oil. The oil and reservoir material were then gently mixed together, using a slim stirring rod inserted through the air injection line.
(vi) the test cell was then secured and all line connections sealed. The guard heaters were then positioned around the test cell.

Operating Procedure*:*

Pressure testing of the inlet and outlet lines to the test cell was performed first, and the test cell was then pressurised to 70 bar with nitrogen to test for leaks. The test cell was then placed into the pressure shell and all connections leak tested again. Air was then injected into the cell, always maintaining the required over pressure in the pressure shell, to minimise the differential pressure. The correct heat loss compensation procedure was selected and the run started under automatic control.

Results and Discussion

ARC tests:
The experimental conditions for the four ARC tests are given in Table 1.

Clair Medium Heavy Oil (19.8 °API): the exothermic reaction trend is shown in Fig. 3**.** The HWS procedure was started at 90 °C. The LTO region occurs below 200 °C and exhibits a gradually increasing temperature, starting at the onset for LTO reactions, at 162.5 °C. The onset temperature is much higher than the original reservoir temperature, since it is greatly influenced by the high water saturation, Sw=50%. Current water flooding operation in the Clair field could conceivably increase the water saturation to around 35%, if oil recovery is limited to 15-20%. The very rapid rise, starting at about 205 °C, is due the establishment of a secondary reaction zone within the gas phase, above the liquid oil-sand sample. Light hydrocarbon components are vaporized from the oil into the flowing gas phase, reaching a lower limit of flammability and

then igniting. There is also a corresponding increase in the test cell pressure, by over 30 bar. A change in reaction regime occurs at 300 °C, as identified by the change in slope of the exotherm. This signifies the transition to full combustion, or bond scission reactions. The automatic cut-off on the equipment limits the maximum temperature to below 500 °C. After Tmax, the temperature falls as the test cell is allowed to cool down.

The self-heat rate (SHR) for the exothermic reaction is shown in Fig. 4. The sensitivity at the onset of the LTO region is 0.06 °C/minute, which is higher than the 0.02 °C/minute detection limit of the instrument. In the reservoir, it is possible that LTO reactions could, in fact, start at a much lower temperature than 162.5 °C. This is because the reservoir will usually behave more adiabatically than the experiments. The LTO and HTO regions are clearly evident for Clair oil. On a logarithmic-arithmetic plot (which can also be plotted against the log of reciprocal absolute temperature, 1/T), the LTO region appears as an exponential-type curve, signifying Arrhenius kinetics, whereas the HTO or combustion region is essentially constant. The maximum self-heat rate (SHR) is 400 °C/ minute. This is very similar to the value obtained for 31 °API Barrancas light crude oil, under flowing reactor cell conditions. In a closed cell, the SHR for this oil was nearer 1000 °C/minute (3). The transition between the two reaction regions is very evident from this type of plot, from the broad region between 270-300 °C. For light oils, there is some indication that, the broader and smoother this transition, the greater the certainty there is of the reaction transitioning to full combustion. Any sensitivity in this transition region, i.e. less broad, or more fluctuating, especially when the water saturation is high (low oil saturation) and when reservoir rock reactivity is lacking, may evidence poorer exothermicity (8). It is evident from Fig. 4 that there is a very smooth continuity in the exotherm, from very low temperature to very high temperature. Thus, Clair crude oil appears, a good candidate for air injection. This is because the oil composition includes the necessary, complete sequence of individual chemical component to ensure that the exothermicity increases continuously with temperature, with no gaps. (5). Li et al. (6) have shown, using pressurized differential scanning calorimetry (PDSC), that the chemical structure also plays an important part in the oxidation behaviour of crude oils. The final temperature reached by the exotherm is 484 °C, but this is artificially limited to protect the equipment. In practice, the temperature attained in the reservoir will likely reach a higher values, because the reservoir tends to operate more adiabatically than the experiment - unless other factors, such as, reservoir thickness, type of cap rock, etc., have any adverse effect.

Fig. 5 shows the composition of the effluent gas from the test cell. The traces follow the trend of the LTO and HTO reactions. If traced back to earlier times, they would identify the start of LTO reactions, possibly at a lower temperature than detected by the ARC.

The other knowledge of combustion performance that is required for an initial feasibility assessment – fuel availability, air requirement and oil burning characteristics, i.e. ability to sustain a propagating combustion zone, can be obtained, in part, from 1-D combustion tube tests. The advantage of combustion tube tests is that they can be performed at high pressure, using reservoir core. However, they have the disadvantage that they do not replicate the flow behaviour, or saturations, existing in the reservoir. The real burning characteristics will, therefore, be different. Tests in a 3-D combustion cell should more realistic, but they are also very costly at high pressure.

Wolf Lake Heavy Oil (10.3 °API): the trend of the SHR in Fig. 6 is similar to that for Clair oil during the LTO phase, reaching a maximum SHR of 30 °C/ minute. However, the very high SHR transition zone is absent and LTO reactions are first detected at 158 °C, nearly 5 °C lower than for Clair oil. This indicates that Wolf Lake oil is more reactive than Clair oil in the LTO region, even though the reservoir pressure is much lower. Potentially, this is a good indication that self-ignition would be achieved in the reservoir, especially if pre-steaming were employed to raise the temperature near the injection well to, say, above 100 °C. There is a continuous, though less-smooth, transition to combustion , but at a significantly lower SHR. The SHR eventually reaches more than 100°C/ minute, at the end of the test. The period over which significant oxygen is consumed and carbon oxide generated, extends over a longer time interval than for Clair oil (Fig.7). This is probably because of the greater fuel availability during the LTO and combustion periods for the heavier Wolf Lake oil.

Athabasca Tar Sand (8 °API): two tests were conducted on virgin Athabasca Tar Sand, containing the original reservoir matrix and reservoir brine. The previous tests on Clair and Wolf Lake oils used crude oil and clean silica sand, containing 3% kaolinite to simulate the natural activity of the reservoir matrix. The Athabasca tests were performed at lower pressure (40 bar) than for the other two crude oils, and at two different oil saturations. Fig. 8 shows the trend of SHR, starting at 113 °C, with an initial sensitivity of 0.04 °C/ minute. The SHR undergoes a smooth increase during the LTO period, up to 300 °C, reaching a maximum of 25 °C/minute. The SHR for the second test, at So = 0.5 (Fig. 9), shows a very similar trend to that at So=0.8. However, the onset of LTO reactions takes place at a much higher temperature, 147 °C, and is detected at a significantly lower sensitivity, 0.02 °C/minute. The higher temperature for the onset of LTO reactions is probably caused by the increased 'heat sink' effect of the sand matrix and water, because of the smaller amount of oil available for reaction. There is no discontinuity in the exotherm as it transitions from LTO to HTO, but the SHR for the HTO region is quite different. A series of short-duration, high SHR periods can be seen in Fig. 8, starting at 400 °C. At 400 °C, the maximum SHR reaches 200°C/minute, then decays in sequential manner, eventually steadying at 40 °C/minute at the end of the test. This indicates that lighter compounds, produced by thermal cracking reactions, attained sufficient concentration in the gas phase to reach the lower limit of flammability. The same behaviour does not occur at lower oil saturation (So=0.5) because, although thermal cracking reactions still take place, there is less oil to produce the required concentration of cracked lighter components in the gas phase. These periods, when the SHR is very high (Figs. 4,8) are actually very short. Only a few minutes, or less, compared with the much longer LTO period.

ARC and Reaction Rate Parameters:

The key parameters obtained from the measured exotherms for each crude oil are summarized in Table 2**,** together with calculated reaction parameters for the LTO and HTO regions.

The pros and cons of implementing ISC as a secondary recovery method, post-steam injection, need to take into account the effect that lower oil saturation may have on

ignition, and whether there is any alteration in overall exothermicity, particularly affecting transition to combustion and stable combustion front propagation. For Athabasca Tar Sand, reducing the oil saturation from 0.80 to 0.50, significantly increases the onset temperature for LTO reactions - by 34 °C. However, the auto-ignition temperature is apparently reduced, from 350 to 300 °C (Table 2). In the experiment, the oil saturation was adjusted by removing particles from the oil-sand-brine matrix and adding clean sand particles to keep the same sand mass. Xia and Greaves (10) have shown that ignition and stable combustion are possible when in situ combustion is performed following a steam flood operation. They used a 3D sandpack, first performing a Toe-to-Heel Steamflood (THSF), and then following this with THAI – Toe-to-Heel Air Injection In the experiment, the oil saturation and water saturations, post-THSF, were approximately, So = 0.54 and Sw = 0.46, respectively.

The energy evolved during the LTO and HTO periods is shown in Table 3. All of the values for the HTO–combustion region are artificially limited, because of the cut-off for the equipment is set below 500 °C. Therefore, the actual values will be somewhat higher than those reported in Table 3. Nevertheless, to a good approximation, and under similar conditions, but at different pressures, we can say that the heat evolved in both regions is broadly similar for Clair and Wolf lake oil. Surprisingly, for virgin Athabasca (So=0.8), the heat evolved during the LTO period is much higher than for the HTO region. This property is usually more associated with a light crude oil than heavy oil or bitumen. It is a factor which indicates that there is good potential for self-ignition in the reservoir when air is injected. However, there is no indication from the present ARC experiments as to how long the ignition delay will be. This can determined from an 'Isoage' test, where the test sample is left at a specific temperature for a sufficiently long period of time. The second test with So=0.5, causes the heat evolved in the two regions to converge to a similar value.

If we compare the main temperature and SHR characteristics obtained from the ARC tests (Table 2), the following ranking is obtained:

Onset temperature: Athabasca< Wolf Lake< Clair

Auto-ignition temperature: Athabasca>Wolf Lake> Clair

Maximum SHR: Athabasca = Wolf Lake < Clair

Maximum combustion temperature: same (artificially limited), all approaching (or potentially exceeding) 500 °C.

Therefore, although Athabasca Tar Sand is more reactive in the LTO region, i.e. it has the lowest onset temperature, 113 °C, it also has the highest auto-ignition temperature, 350 °C. The onset temperature of 113° is, in fact, closer to what one would expect to see for a light oil (9). Only Clair oil, which has a heavy residue content of about 35%, compared to over 55% for Wolf Lake and Athabasca Tar Sand, has sufficient amount of light (vaporizable) components to exhibit a high SHR (400 °C/minute) in the transition region.

The range of calculated activation energies (E) given in Table 2 enables the following ranking:

LTO region: Athabasca<Wolf Lake< Clair

HTO region: Athabasca>Wolf Lake>Clair

Thus, the onset temperature for start of LTO reactions is aligned with the activation energies for the LTO region, and the auto-ignition temperature is aligned with the activation energies for the HTO region. The low value of E for Athabasca Tar Sand in the LTO region (44.6 kJ/mol) is a further indication of the high oxidation reactivity, i.e. ability to consume oxygen and produce heat. In the HTO region, Athabasca Tar Sand has the highest activation energy in the HTO region (147.2 kJ/mol), so high exothermicity is only possible at high temperatures.

Conclusion

1. From ARC tests at reservoir pressure, Clair medium heavy oil, Wolf Lake heavy oil and Athabasca Tar Sand all exhibit continuous exothermicity trends – ability to transition from LTO to HTO, or full-combustion. Therefore, all three crude oils are potentially good candidates for in situ combustion.
2. The onset temperature for the start of LTO reactions was lowest for virgin Athabasca Tar sand. Its relatively low value (113 °C) is quite close to that observed for light oils in a deep, high temperature reservoirs.
3. The low value of the activation energy for Athabasca Tar Sand in the LTO region (44.6 kJ/mol) indicates high oxidation reactivity, and has the potential, therefore, to achieve auto-ignition eventually, when air is injected into the reservoir, i.e. if the reservoir temperature is increased sufficiently for intense close to LTO reaction to occur.

Acknowledgement

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Table 1 – Experimental conditions

Experiments	Initial pressure (bar)	Flow rate (ml/min)	Oil saturation %	Water/brine saturation %	Rock weight gm
Clair	202	120	50	50	5.93
Wolf Lake	102	120	50	50	5.93
Athabasca 1	40	120	80	~20%	7.0 with oil + brine
Athabasca 2	40	120	50*	~20%	7.0 with oil + brine

*adjusted by removing sand particle and adding clean sand particles, compared to Athabasca 1 test

Table 2 - Summary of PhiTech2 ARC tests results and kinetic parameters

Oil	T Onset (°C)	T Auto-Ignition (°C)	T Max (°C)	Max Self-heat rate (°C/min)	LTO				HTO			
					Temp. Range	E kJ/ g mol	ln(A) ln(1/sec)	n	Temp. Range	E kJ/mol	ln(A) ln(1/sec)	n
Clair	162.50	205.00	485.00	400.00	162-206	109.00	19.11	0.00	308-484	64.00	5.96	0.00
Wolflake	158.00	300.00	480.00	200.00	158-300	77.50	10.99	0.00	300-480	82.30	9.90	0.00
Athabasca 1	113.00	350.00	480.00	200.00	113-350	44.60	1.15	0.00	350-480	147.24	20.60	0.00
Athabasca 2	147.00	300.00	480.00	30.00	147-311	74.45	9.76	0.00	327-480	73.54	8.16	0.00

Table 3 - Energy Evolved

Oil	Induction Period (J)	Auto-ignition Period (J)	LTO Overall (J)	HTO Overall (J)
Clair	878	2128	3006	3636
Wolf Lake	2946	415	3361	3319
Athabasca 1	4855	428	5282	2566
Athabasca 2	3367	328	3695	3141

Specific heat of all crude oils taken as 2.14 kJ/kg °C
Specific heat of sand and core materials taken as 1.0 kJ/kg °C
Sand grain density = 2500 kg/m^3

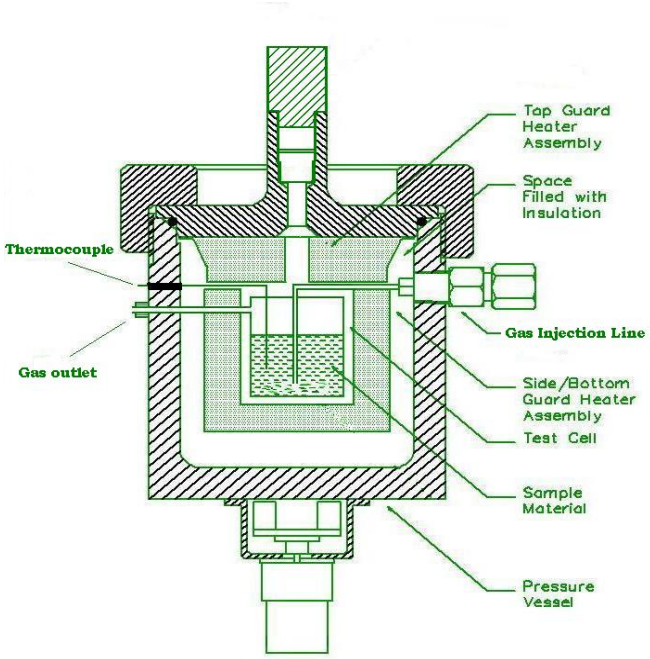

Figure 1 – Pressure containment vessel surrounding test cell

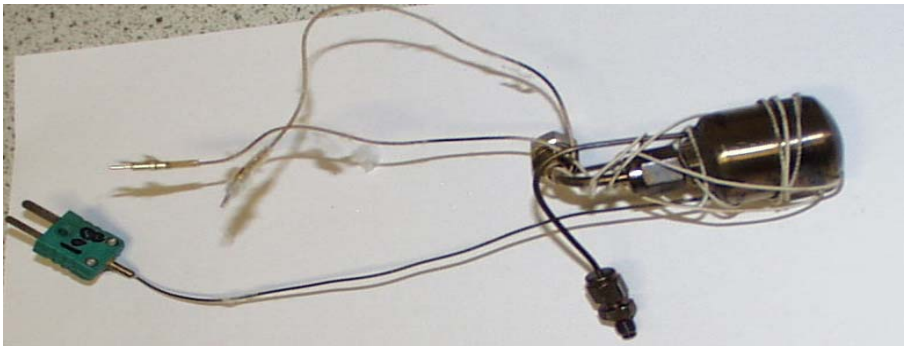

Figure 2 - Test Cell

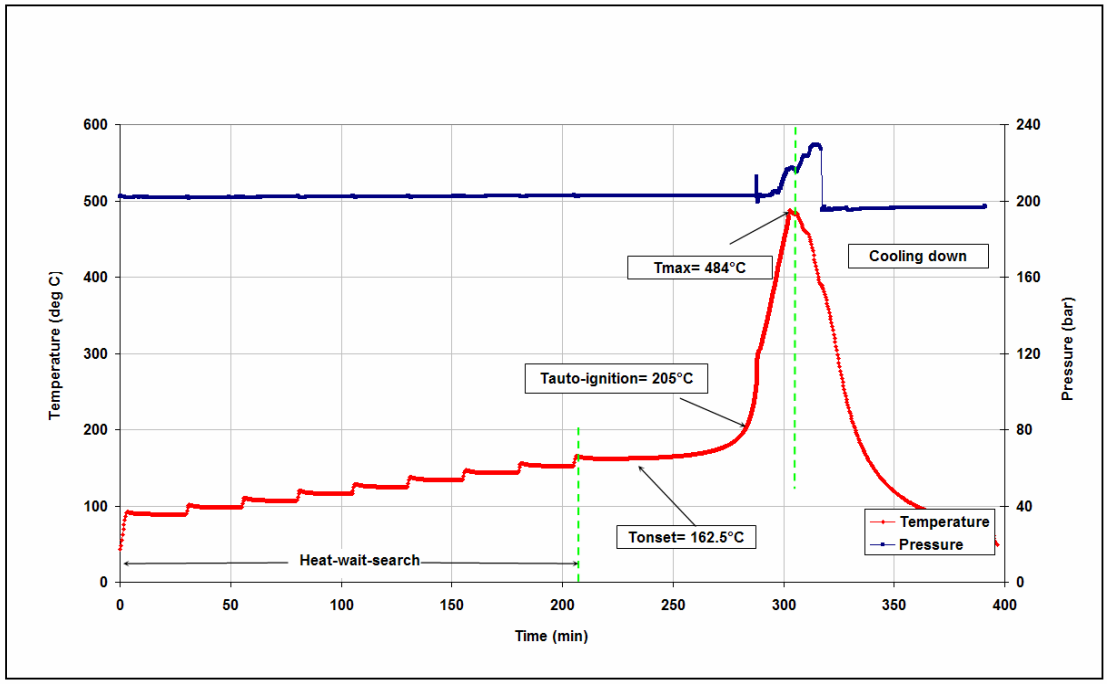

Figure 3 - Temperature vs. time (Clair oil at 202 bar)

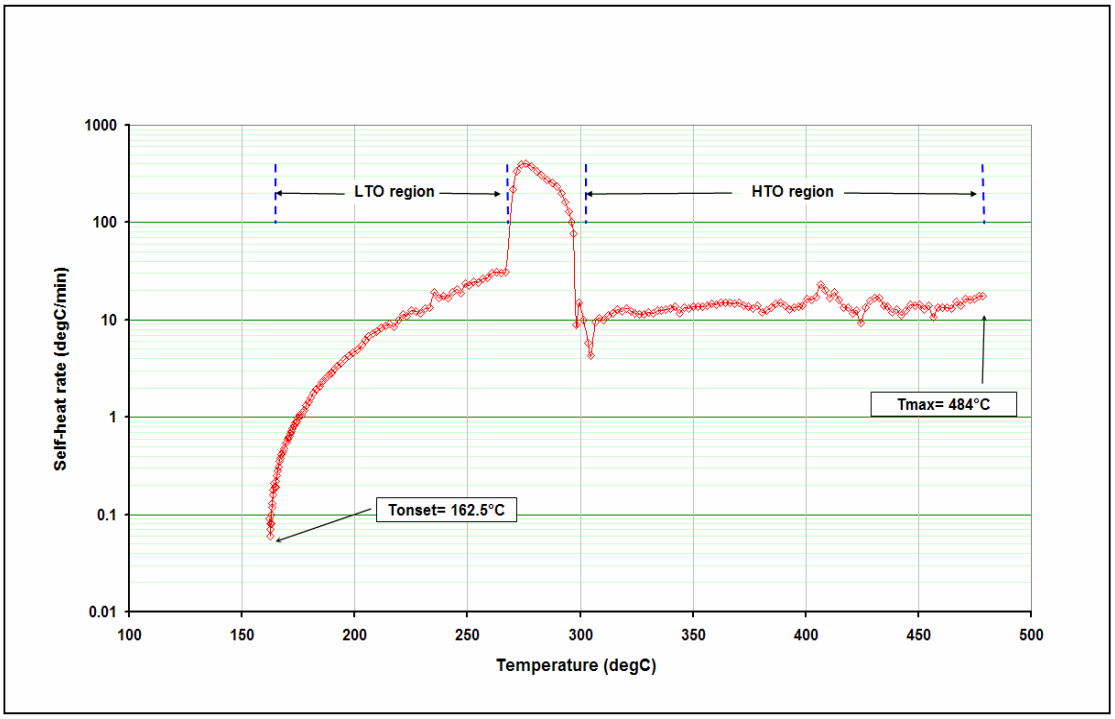

Figure 4 - Self-heat rate vs. temperature (Clair oil + rock at 202 bar)

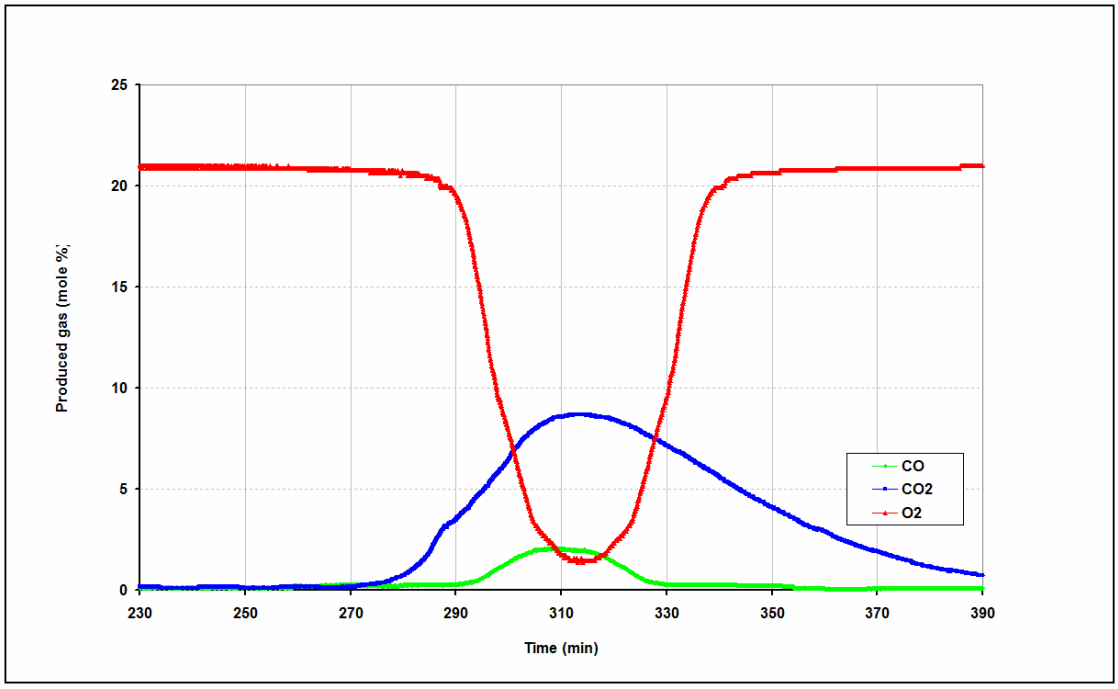

Figure 5 - Produced gas composition (Clair oil + rock at 202 bar)

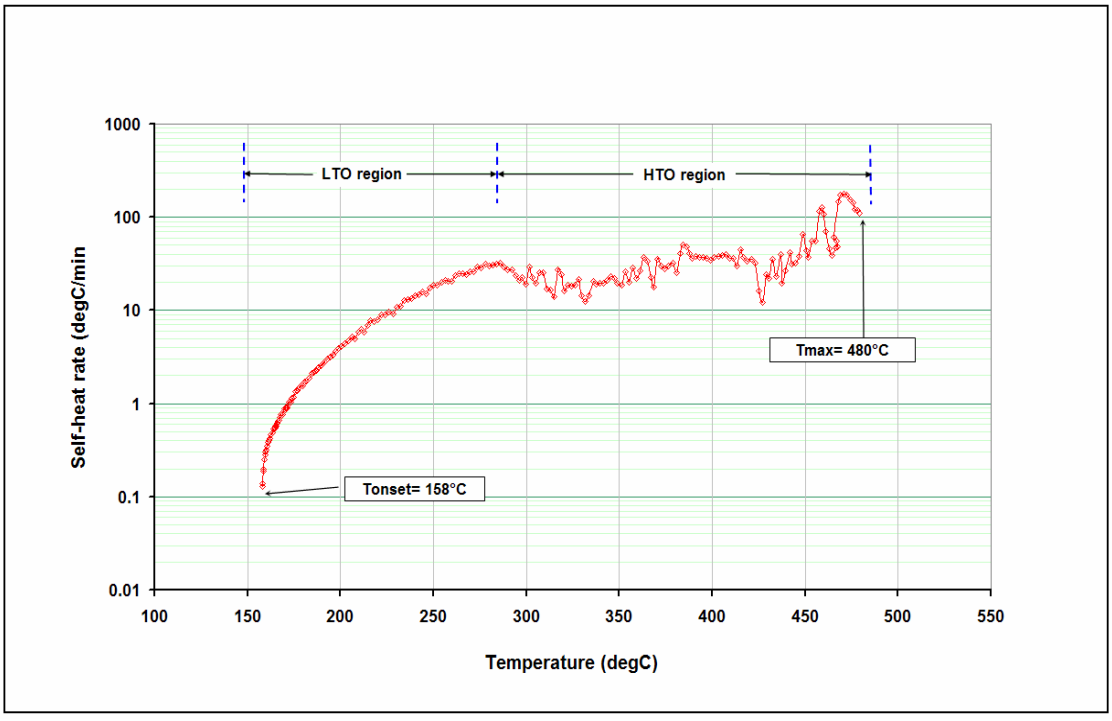

Figure 6 - Self-heat rate vs. temperature (Wolf Lake Oil at 102 bar)

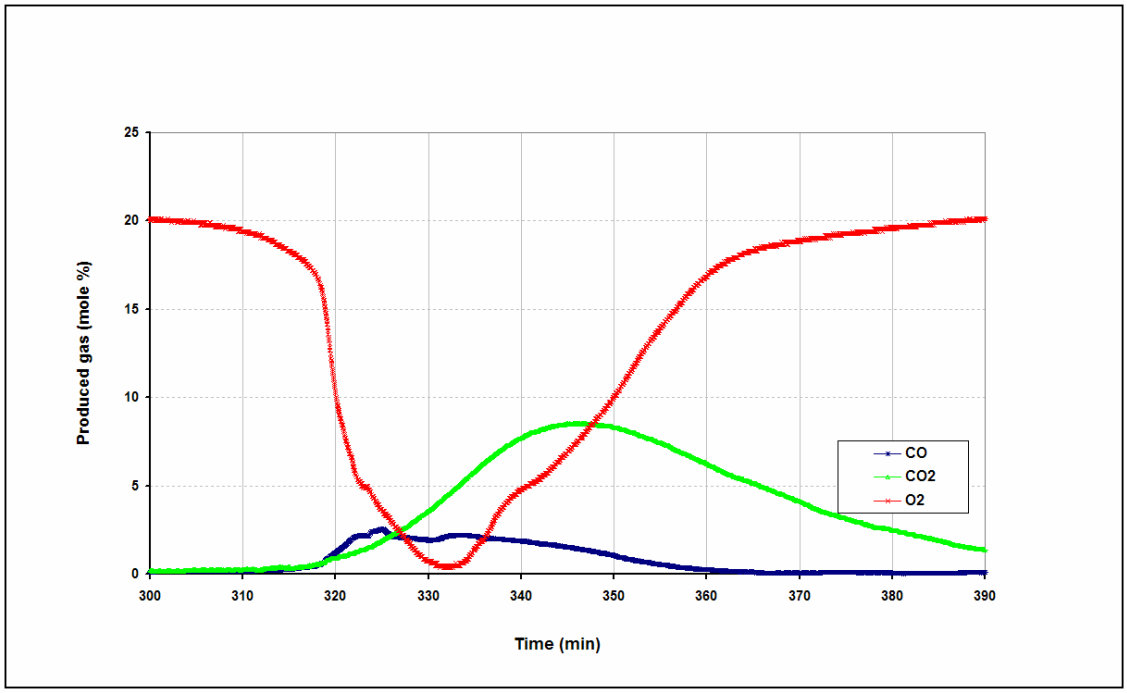

Figure 7 - Produced gas composition (Wolf Lake Oil at 102 bar)

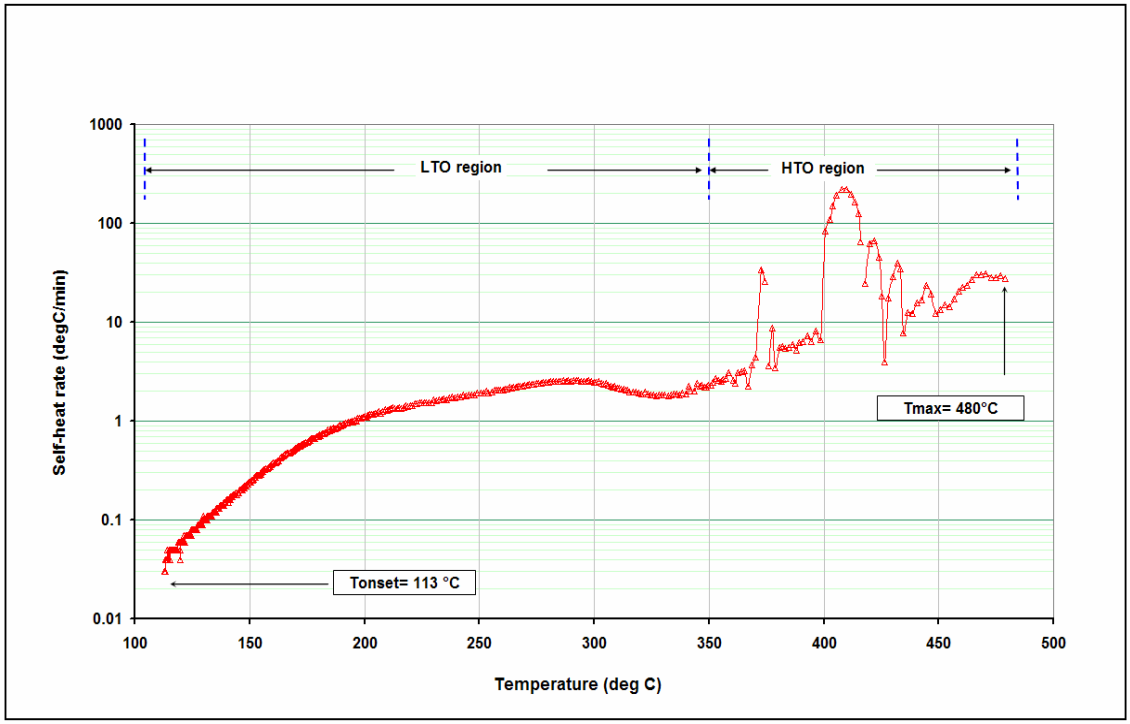

Figure 8 - Self-heat rate vs. temperature (Athabasca Tar Sand at 40 bar, So=0.8)

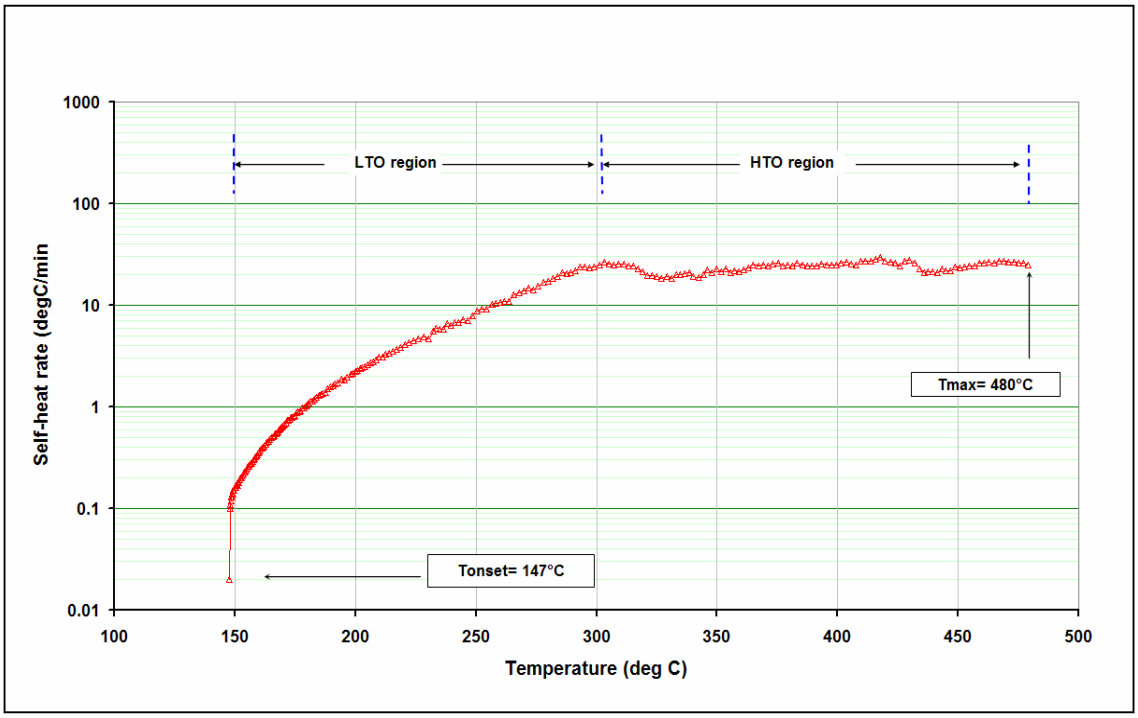

Figure 9- Self-heat rate vs. temperature (Athabasca Tar Sand at 40 bar, So=0.5)