

# **The effect of un-saturates on low-temperature oxidation of crude oil**

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## **Abstract**

Low-temperature oxidation (LTO) of four Arabian crudes as well as blends of naphtha with a super-light crude was investigated employing differential thermal analysis. The mass fraction of un-saturates in the reactants varied between 0.2 and 0.9.

All reactants showed LTO peaks between 230 and 264 °C; heat flow at the peak, however, varied widely. The data revealed a clear increase in LTO-generated heat as the reactant's content of un-saturates increased. The lightest crude with 51.1 °API gravity and un-saturates fraction of 0.2 showed the least LTO reactivity.

It is, therefore, concluded that the un-saturates content of a crude is an influential factor in its LTO tendency and, thus, its potential for spontaneous ignition and other enhanced-recovery techniques that rely on LTO.

*Keywords: un-saturates; oxidation; thermal analysis*

## **1. Introduction**

Low-temperature oxidation (LTO) is a slow, mildly exothermic reaction, which is prompted whenever air contacts crude oil at temperatures normally encountered in petroleum reservoirs. The success of a number of processes that involve injecting air into a reservoir depends on the oil's LTO reactivity. When combustion of the oil is the main process mechanism, LTO-prompted spontaneous ignition of the oil is highly desirable. On the other hand, when spontaneous ignition must be avoided such as in improved recovery from light-oil reservoirs

by air injection [1] or when air is injected for sand consolidation purposes [2] moderate LTO reactivity becomes necessary.

LTO reactions of crude oil prevail at temperatures below 300 °C producing mostly water and oxygenated hydrocarbons such as alcohols, aldehydes, ketones, carboxylic acids and hydroperoxides [3]. It has been concluded that light crudes are generally more susceptible to LTO [1,4] because of their relatively high hydrogen content [4]; another study [5], however, found that this conclusion might not be justified. More recently, the aromatics and resins in bitumen and heavy crudes have been found to be the most susceptible to LTO, while the saturates are the least affected [6,7]. Moreover, by increasing the asphaltene content of an oxidized oil, LTO increases the oil's density and viscosity; such increases were also correlated with the extent of oxidation [8]. Light crudes, however, show minor increases in density and viscosity [8]. Since LTO is a gas-liquid reaction, its rate is accelerated by a larger contact area provided by finer grained rock [9]. The presence of clays and/or metallic derivatives either in the rock or in the oil also has catalytic effects on LTO reactions [3].

Detailed information on the oxidation characteristics of a crude oil can be acquired employing an oxidation reactor [1,10]. However, semi-quantitative data can be obtained by differential thermal analysis [5,9,11]. In this technique, a small sample of the oil is weighed continuously as it is heated at a constant rate of temperature rise while exposed to air flow. The resulting curves of the sample's mass (thermogram) and the time-rate of mass loss (differential thermogram), both versus temperature, provide valuable information on the rate at which evaporation or oxidation reactions within the sample take place. Simultaneously, the rate of heat generation, or absorption, within the sample is also measured by comparing its temperature with that of a thermally inert substance undergoing the same heating program.

The rate of heat flow, expressed in microvolts, versus temperature (heat flow curve) helps identify evaporation and oxidation regimes within the temperature range of interest.

In this study, LTO of four Arabian crude oils as well as blends of naphtha with one of the four oils ( a super-light crude) was investigated employing differential thermal analysis. This study was prompted by a previous study [12] in which the super-light crude failed to self-ignite under a range of conditions.

## **2. Experimental work**

**Materials.** The main subject of this study was a 51.1 °API-gravity, super-light crude oil (Oil A) from central Saudi Arabia. Three other Saudi Arabian oils were also tested: an Arabian-heavy crude from the northeast (Oil B), an Arabian-extra-heavy crude from the east (Oil C), and an Arabian-medium crude from the southeast (Oil D). Six blends of analytical-grade naphtha with Oil A were also tested. The purpose of blending with naphtha was to increase the oil's content of un-saturates. Table-1 lists the properties and analyses of the four crudes and the naphtha while Table 2 lists blend compositions. Analyses of the crudes were determined by the SARA group test procedure. In all tests, the crude (or blend) was mixed with sand produced from Oil A reservoir and recovered from a field separator.

**Setup.** A LABSYS model TG-DTA12 thermal analyzer that performs both thermogravimetric analysis and differential scanning calorimetry was used. The system consists of three basic components: the measuring chamber, the recording and control cabinet and the data acquisition system. The measuring chamber is equipped with two heating ovens in which the oil sample and reference sample crucibles are housed separately. Attached to each crucible is an ultra-sensitive thermo-balance that monitors changes in both weight and temperature of the

sample as heating progresses. Both ovens undergo the same heating program and are operated at atmospheric pressure.

**Procedure.** Each run begins with placing about 100 mg of the oil/sand mixture in the sample crucible. The oil content in the mixture is about 6.5 mg. The reference crucible contains a sample of inert gamma-alumina with identical weight to the mixture. Air is then passed through the ovens at a constant rate of 100 scc/min; at the same time heating is started from room temperature up to around 700 °C at a rate of 10 °C/min. At the end of each run, the analyzer provides a printout showing three curves: the thermogram (TG), the differential thermogram (DTG) and the heat flow curve (HFC), all versus temperature.

### **3. Results and discussion**

Ten runs were conducted: one on each of the four crude oils as well as the 6 blends. Figure 1 shows the results for the super-light crude (Oil A). The DTG indicates continuous loss in the sample's mass from room temperature (22 °C) to the termination temperature of 700 °C with two distinct peaks. The first peak (at 230 °C) is caused by evaporation, which normally dominates mass loss below 300 °C [5,9,11]. LTO should be also active around the peak temperature, yet its effect on mass loss with Oil A is not as marked as with other crudes [9,11]. In those two studies, LTO caused an increase in mass, which was manifested by significant leveling in the DTG just before the peak. Occurrence of LTO, however, can be inferred from the HFC for Oil A shown in the same figure. Although evaporation is mildly endothermic, exothermic LTO takes over beyond 100 °C causing the small hump in the HFC at 243 °C with a value of about 11 microvolts ( $\mu\text{V}$ ). For comparison purposes in this study, the first peak in the DTG is considered a LTO peak and the temperature and heat flow corresponding to it are adopted as measures of the oil's LTO reactivity.

The second peak in the DTG around 400 °C is caused by high-temperature oxidation (HTO) of the heavy residue, composed mainly of products of cracking and coking. The small magnitude of the this peak is consistent with the low un-saturates content of Oil A (19.94 wt%), an observation collaborated by the TG of Oil A (not shown) which indicates nearly 75% loss in oil mass by the onset of HTO around 320 °C. Highly exothermic HTO, however, generates enough heat to cause the 22.5- $\mu$ V peak in the HFC at 400 °C. Since HTO begins generating significant heat before reaching that peak temperature, the prominent 22- $\mu$ V middle peak in the HFC observed at 350 °C is the combined contribution of both LTO and HTO over the transition temperature range. Some investigators [9] attributed this middle peak to cracking/coking reactions.

The thermal analysis results of Oil A are quite different from those of highly asphaltic Oil C, which are shown in Fig. 2. While the LTO peak occurs at 261 °C, the corresponding heat flow is 16.8  $\mu$ V - one and a half times larger than that of Oil A. In addition, the rate of mass loss at this peak for Oil C is much slower, which indicates more vigorous LTO and/or milder evaporation. The increased heat generation at the LTO peak is attributed to the larger fraction of un-saturates in Oil C, a fraction shown to be the most susceptible to LTO. Such larger content of un-saturates also explains the 82% increase (compared to Oil A) in heat flow at the HTO peak for Oil C, as more fuel is available for this reaction.

For comparison purposes, the HFC's of the 4 crudes and the 6 blends are shown in Figs. 3 and 4, respectively. It is interesting to note that among the three asphaltic crudes only Oil D, the lightest one and with the largest aromatics fraction, shows marked endothermicity during early evaporation. For the blends, endothermicity is only seen with Blends 1, 2 and 3 with Blend 1 (80% aromatics) displaying the maximum.

LTO peak temperatures of the 10 fluids are plotted versus the content of un-saturates in Fig. 5. A clear trend is observed indicating elevated peak temperatures with increased content of un-saturates. A similar trend is observed with the heat flow at the LTO peak, Fig. 6, where the heat flow nearly doubles over the range of un-saturates content indicating a definite correlation between the two parameters. Such correlation probably explains the poor LTO tendency of the super-light crude (Oil A) observed in the earlier study [12]. In that study spontaneous ignition of the crude could not be achieved under a wide range of conditions, and it had been concluded that low rate of heat generation by LTO prevented the temperature of the crude oil/sand mixture from rising to ignition levels. Investigating the reason behind such an apparent anomaly lead to the present study. It is interesting to note at this point that the LTO and HTO peak temperatures of Oil A match those of a Louisiana crude [5] whose composition is almost identical to Oil A.

While the results of this study do not provide an empirical correlation on the effect of un-saturates on LTO reaction, qualitative assessment of such an effect can be construed. Since the shift in peak temperature (on the absolute temperature scale) is not relatively great, one can speculate that the un-saturate content does not alter the LTO activation energy significantly. However, the heat generated by LTO per unit mass of oil appears to increase steadily with the content of un-saturates especially beyond 50% for the fluids tested.

#### **4. Conclusions**

Based on the results of this study, the following conclusions can be made:

- (1) The un-saturates (aromatics, resins, asphaltenes) content of a crude oil appears to have an influential effect on the oil's propensity for LTO.
- (2) A larger content of un-saturates causes the oil to generate more heat during LTO with a relatively small elevation in LTO-peak temperature.

- (3) Endothermicity during the evaporation stage appears to be related to the oil's content of aromatics.
- (4) Incremental oil recovery from highly paraffinic, light oil reservoirs by air injection might not be significant due to potentially poor LTO reactivity.
- (5) Chances for spontaneous ignition in highly paraffinic, light oil reservoirs could be enhanced by enriching the oil in the near-wellbore area with aromatic/asphaltic material.

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Table 1: Properties of Oils and Naphtha.

<b>Fluid</b>	<b>°API @ 15 °C</b>	<b>Viscosity (cp) @ 24 °C</b>	<b>Composition (wt%)</b>				<b>Total Un- Saturates</b>
			<b>Saturates</b>	<b>Aromatics</b>	<b>Resins</b>	<b>Asphaltenes</b>	
Oil A	51.1	1.77	80.06	19.47	0.29	0.18	19.94
Oil B	17.9	6503	13.22	54.24	28.44	4.10	86.78
Oil C	22.2	93.3	9.32	60.23	15.46	14.99	90.68
Oil D	32.8	8.2	16.88	75.68	4.04	3.40	83.12
Naphtha	31.9	0.76	3.80	95.00	0.70	0.50	96.20

Table 2: Oil A/Naphtha Blend Compositions.

<b>Blend</b>	<b>Oil A (wt. %)</b>	<b>Naphtha (wt. %)</b>	<b>Un-Saturates* (wt. %)</b>
1	19.9	80.1	81.02
2	33.2	66.8	70.88
3	46.4	53.6	60.82
4	59.6	40.4	50.75
5	72.8	27.2	40.68
6	86.1	13.9	30.54

\* Blend content of un-saturates as computed from compositions of Oil A and naphtha.

Fig. 1: Differential Thermal Analysis of Oil A.

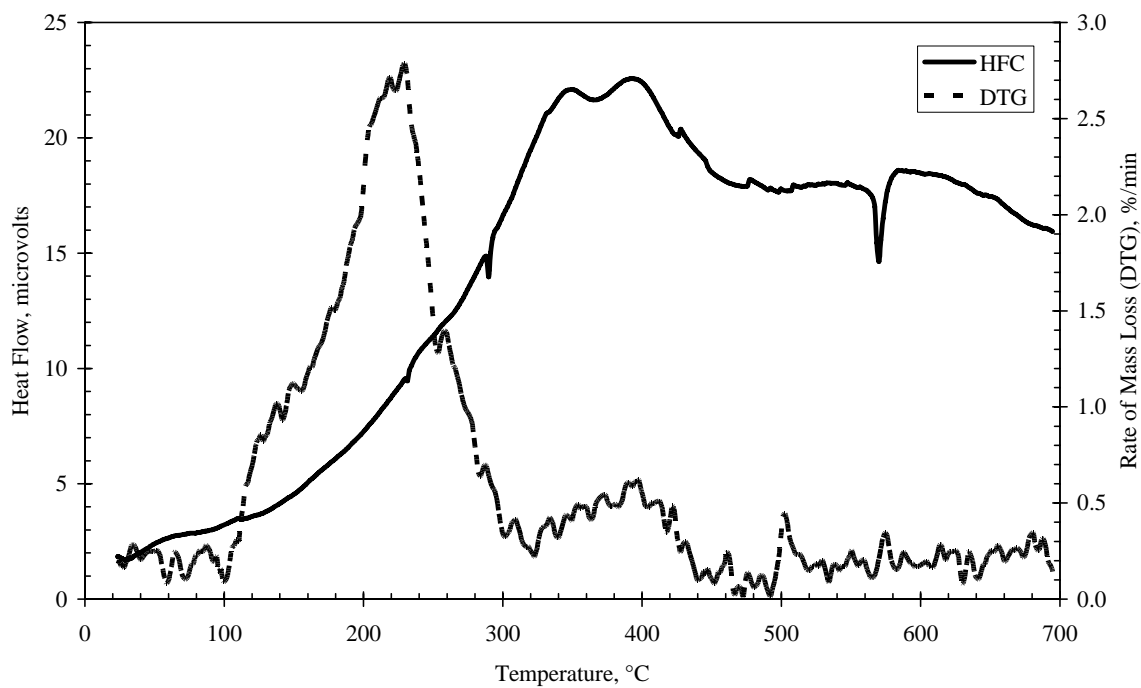


Fig. 2: Differential Thermal Analysis of Oil C.

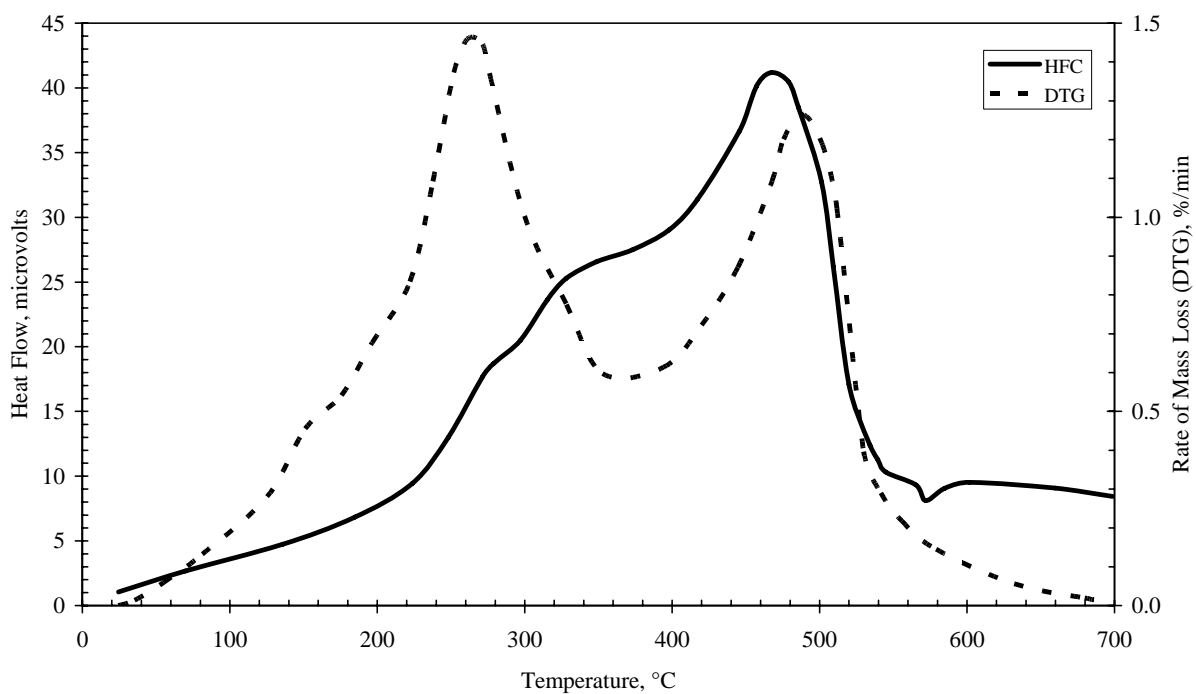


Fig. 3: Heat Flow Curves of Four Crudes.

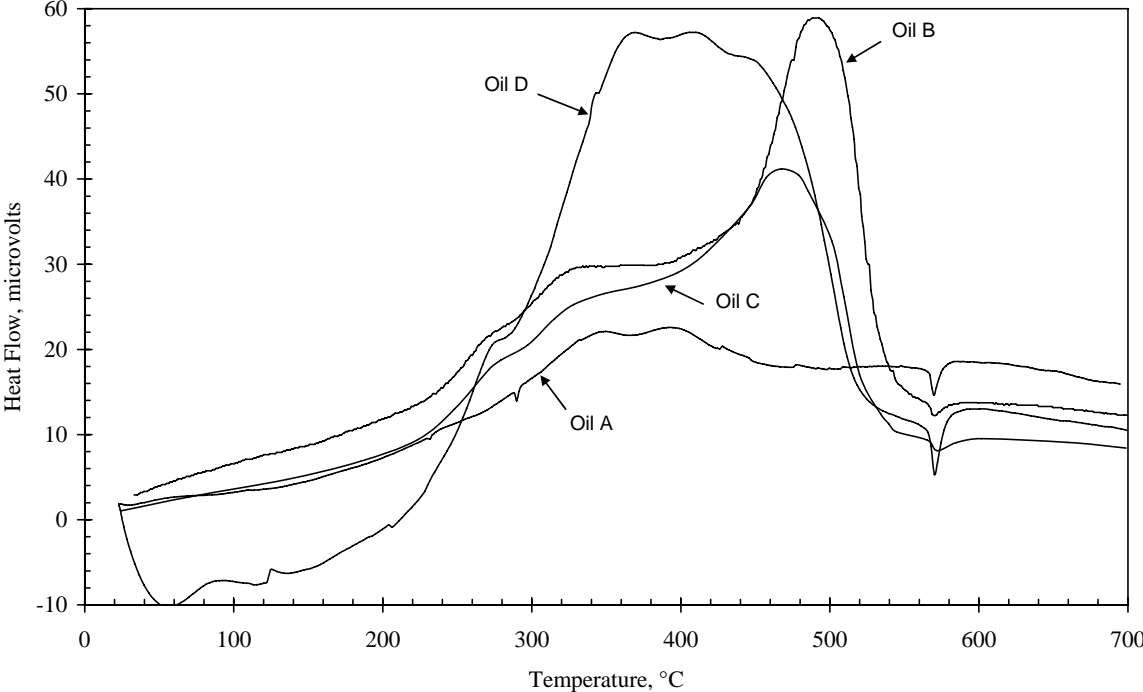


Fig. 4: Heat Flow Curves of Six Blends.

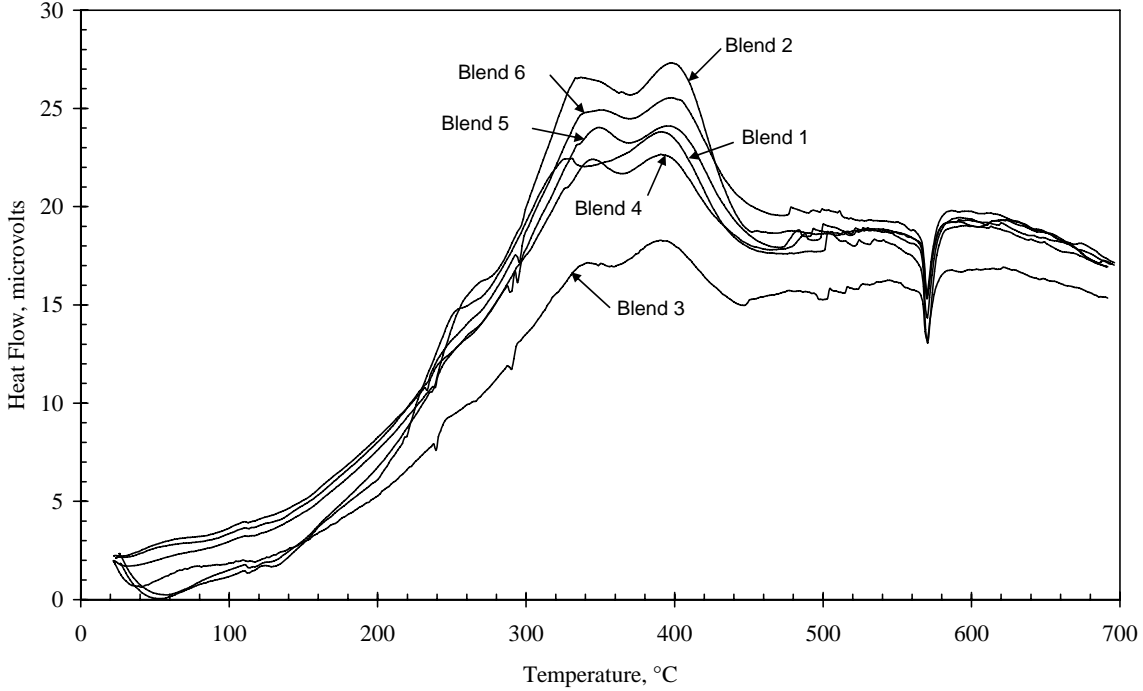


Fig. 5: Effect of Un-Saturates Content of the Fluid on its LTO-Peak Temperature.

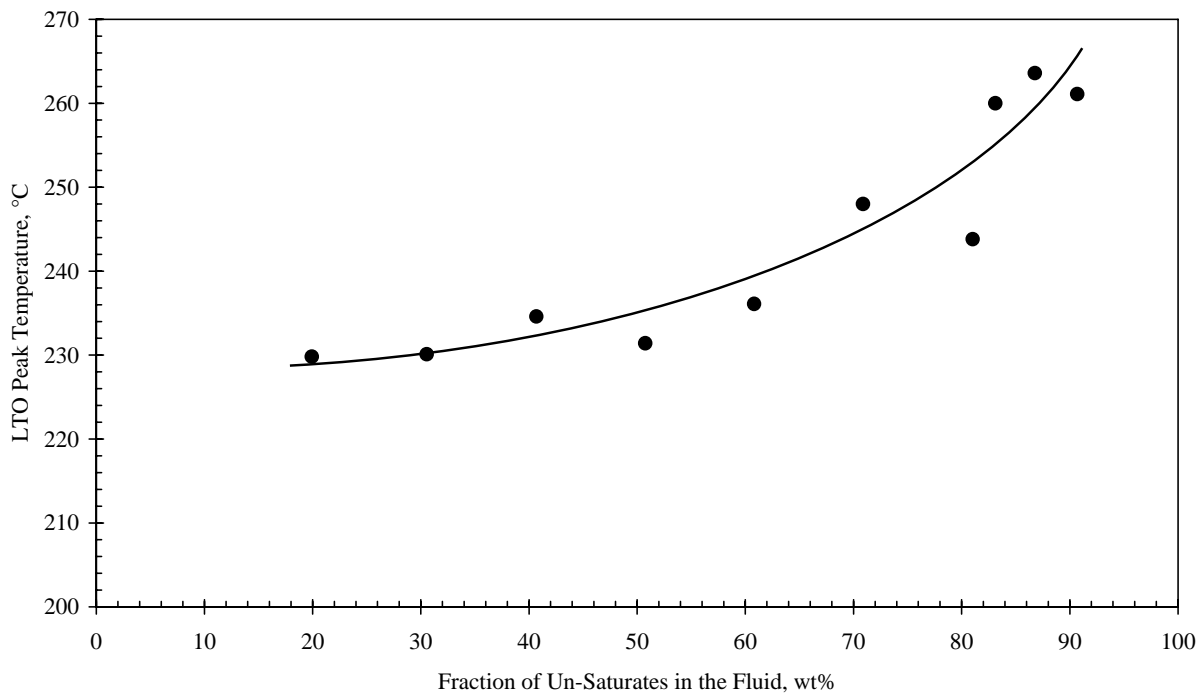


Fig. 6: Effect of Un-Saturates Content of the Fluid on Heat Flow at the Fluid's LTO-Peak Temperature.

