THE EFFECT OF PRESSURE ON OXIDATION KINETICS OF TAR FROM A TARMAT RESERVOIR

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ABSTRACT

The oxidation kinetics of a tar with physical and chemical characteristics similar to those of a reservoir tar were studied employing a variable-temperature oxidation reactor. Mixed with clean, loose sand, the tar showed oxidation behavior typical of heavy crudes with LTO and HTO peaks in oxygen consumption. Higher pressures caused larger LTO-oxygen consumption, lower HTO-oxygen consumption, lower HTO-peak temperatures, higher apparent H/C ratio of fuel, and lower HTO activation energy. All these effects are attributed to suppression of light-end evaporation at low temperatures. Compared with clean sand, natural crushed-core material promoted LTO of the tar but did not alter HTO parameters significantly. With HTO-peak temperatures and activation energies above 500 ºC and 100 kJ/mol, respectively, the tar is not expected to provide for sustained in-situ combustion in the reservoir.

INTRODUCTION

Tarmat is a loosely defined term ascribed to a layer of very viscous tar or bitumen that exists around the periphery of some oil reservoirs, usually at the oil/water contact (Tripathy, 1988). Reservoirs displaying various extents of this feature are termed tarmat reservoirs. Such reservoirs are encountered throughout the world and, particularly, in the Middle East where a typical case is the Arab-D reservoir of the super-giant Ghawwar field (Osman, 1985). The tar deposit in the Uthmaniya area only of this carbonate reservoir is estimated at 400 million m^3. The immediate consequence of the tarmat is deprivation of the reservoir's oil zone of adjacent aquifer support. In severe cases where the tarmat totally surrounds the oil zone, the reservoir behaves like a finite lens with rapid drop in pressure accompanied by an alarming increase in production gas/oil ratio during primary depletion (Osman, 1985). In other cases where the tar has some mobility, the pressure differential across the tarmat could build up to a level that might cause the tar seal to beak down rather abruptly allowing severe water coning into nearby wells.

Methods for removal or dissipation of the tarmat have been investigated in the laboratory but not field tested yet. One study involved water injection below the tarmat (Abu-Khamsin et al., 1993). This simple technique proved ineffective as extremely high pressure gradients were required to breach the tar layer, and significant amounts of oil were bypassed by water fingering through the tarmat leading to poor oil recovery. Another study experimented with injecting various solvents, all driven by hot water (Okasha et al., 1998). The results showed efficient displacement of tar at an optimum slug size for each solvent; and maximum oil recovery was achieved when the optimum solvent slug was injected in portions alternating with hot water. The economics of the process, however, are yet to be evaluated by a field test. It is expected, though, that well-bore heat losses would render such thermally-assisted, miscible displacement technique rather ineffective in the deep reservoirs of the Middle East. This leaves in-situ combustion with its high heat efficiency and low cost as a viable, alternative solution to this problem.

In-situ combustion has been applied successfully for a number of heavy oil reservoirs. Description, mechanisms and requirements of the process are well documented in the literature (Butler, 1991) and need not be repeated here. A crucial factor that influences performance of in-situ combustion is availability and reactivity of the fuel. Insufficient fuel deposition ahead of the combustion front or a slow rate of high-temperature oxidation (HTO) within the front deprive the front of the heating rate necessary to sustain the process leading to premature extinction. A summary of the effects of various process variables on the amount and nature of the fuel was provided (Abu-Khamsin et al., 1988). While medium and heavy crudes usually satisfy the fuel requirement (Alexander et al., 1962), and tar is expected to conform to this rule, the rate of HTO of the fuel as dictated by oxidation kinetics becomes the controlling factor (Shahani and Hansel, 1987).

Under ideal conditions, the HTO reaction proceeds in the following manner:

$$\text{Fuel} + O_2 \longrightarrow CO + CO_2 + H_2O \qquad (1)$$

The rate of this gas-solid reaction is modeled by a simple kinetic equation:

$$R_{HTO} = k_{HTO} P_{O2}^{m} C_f^{n} \quad (2)$$

Where R_{HTO} is the rate of HTO of fuel (g per cm^3 of rock per s), k_{HTO} is HTO reaction rate constant (consistent units), P_{O2} is partial pressure of oxygen (Pa), C_f is fuel concentration (g per cm^3 of rock), m is reaction order with respect to oxygen, and n is reaction order with respect to fuel. As governed by Arrhenius law, the HTO reaction rate constant is expressed as:

$$k_{HTO} = A \exp(-E_{HTO} /RT) \quad (3)$$

Where A is a frequency factor (consistent units), E_{HTO} is HTO reaction's activation energy (kJ/mol), R is the universal gas constant, and T is temperature (°K). As Equs. 2 and 3 indicate, values of four kinetic parameters (A, E_{HTO}, m and n) are required before the rate of HTO can be estimated and, thus, feasibility of combustion can be assessed. A survey of published kinetic data as well as a report on new data for mostly heavy crudes was provided (Fassihi et al., 1984, p. 399). In that data, order n varied slightly around unity but order m showed wide variation. Wider variation was found with A, but most investigators presume it to depend upon the specific surface area of the porous medium. E_{HTO} is largely a property of the fuel or its parent oil (Fassihi et al., 1984, p. 399) with more carbonaceous fuels showing higher energies. Given sufficient fuel, combustion can proceed smoothly at normal combustion temperatures if E_{HTO} is low to medium in magnitude. If this energy were high, a large A, a higher oxygen pressure or a higher combustion temperature would be needed to carry the process forward. Since heavier crudes tend to show higher E_{HTO}, based on this parameter only tars would make poor candidates for in-situ combustion.

HTO reaction kinetics are studied employing variable-temperature oxidation reactors operated under a wide range of conditions. In such reactors, progress of various oxidation reactions is followed by monitoring the reactor's temperature and composition of its effluent gas. A graphical technique to extract HTO kinetic parameters from the reactor's data was described (Fassihi et al., 1984, p. 408). Such approach has been adopted in this study whose purpose was to investigate HTO kinetics of a tar similar in characteristics to the tar deposit found in the Arab-D reservoir of Ghawwar field. The results would help provide a preliminary assessment of the feasibility of in-situ combustion as a tar displacement method.

EXPERIMENTAL WORK

Materials

Due to the scarcity of reservoir tar samples, the tar used in this study was prepared by distilling Ghawwar Arab-D crude under nitrogen atmosphere to yield a residue of physical and chemical properties similar to the reservoir tar. Such approach is justified by results of mass spectroscopy and other tests, which showed that the natural tar and Ghawwar oil are chemically similar and genetically related, and that the tar had formed from the oil by gas de-asphalting over geologic time (Riley et al., 1977). Table 1 lists physical and chemical properties of the prepared tar as well as average properties of 6 tar samples obtained from 3 wells in Uthmaniyah area of Ghawwar.

Table 1: Physical and Chemical Properties of Tars.

Property	Tar Source	
	Prepared	Reservoir*
Density @ 15 °C, g/ml	0.922	0.976
Density @ 104 °C, g/ml	0.873	0.919
Viscosity @ 15 °C, cP	10322	12400
Viscosity @ 104 °C & 2000 psia, cP	23	
Sulfur content, wt%	3.25	3.75
Nitrogen content, wt%	0.25	
Carbon content, wt%	81.8	82.2
Hydrogen content, wt%	11.8	11.5
Atomic Hydrogen/Carbon ratio	1.73	1.68
Saturates, wt%	32.8	30.0
Aromatics, wt%	32.4	34.8
Resins, wt%	9.0	9.6
Asphaltenes, wt%	25.8	25.6

* Average of 6 samples from 3 wells in Uthmaniyah, Ghawwar.

Two types of porous media were used: clean dune sand and crushed Arab-D core material both thoroughly washed with distilled water and cleaned with toluene. Sieve analyses of both media is listed in Table 2.

Setup

Figure 1 shows a schematic of the apparatus, which consisted of gas supply and control, oxidation reactor and heating oven, reactor temperature measurement, a combustion analyzer for effluent gas analysis, and a data acquisition system.

The oxidation reactor (Fig. 2) was made of a thick-walled, stainless steel pipe measuring 12 cm (length) x 3.18 cm (OD) x 2.54 cm (ID). The pipe was sealed at both ends by flanges and copper O-rings. A 1.6-mm OD, stainless steel tube fitted through the top flange and reaching down to 2 cm above the reactor's bottom flange served as a thermowell, which housed a thermocouple.

Table 2: Sieve Analyses of Porous Media.

Screen Mesh Size	Wt% Retained	
	Dune Sand	Crushed Core[*]
30	0	0
40	0.39	0.88
50	60.10	23.72
60	20.11	14.84
100	6.62	18.93
140	5.11	11.34
200	6.94	12.78
Fines	0.73	17.51
	100.00	100.00

[*] Cores from Arab-D reservoir, Ghawwar.

Procedure

A typical run began by packing a mixture of about 2 g of tar and 25 g of porous medium into the reactor. About 20 g of clean sand were placed on top of the mixture to help preheat and distribute air flow. The reactor was then assembled, pressure tested with nitrogen, placed into the oven, and connected to the flow system.

After pressurizing with nitrogen to the desired level and attaining an initial temperature of 100 ºC, the oven's heating program was started at a rate of about 70 ºC/h. Simultaneously, air flow through the reactor was initiated and maintained at 760 std. ml/min. During a run, the tar-sand mixture's temperature and combustion analyzer readings were recorded continuously. A run was terminated

Legend

1. Pressure gauge
2. Valve
3. Two-way valve
4. Drying bed
5. Gas flow controller
6. Oven
7. Pre-heating coil
8. Reactor
9. Thermowell
10. Thermocouple
11. Ice bath
12. Back-pressure regulator
13. Acid scrubber
14. 2-micron filter
15. Gas flow meter
16. Combustion analyzer
17. Thermocouple reader
18. Data acquisition system

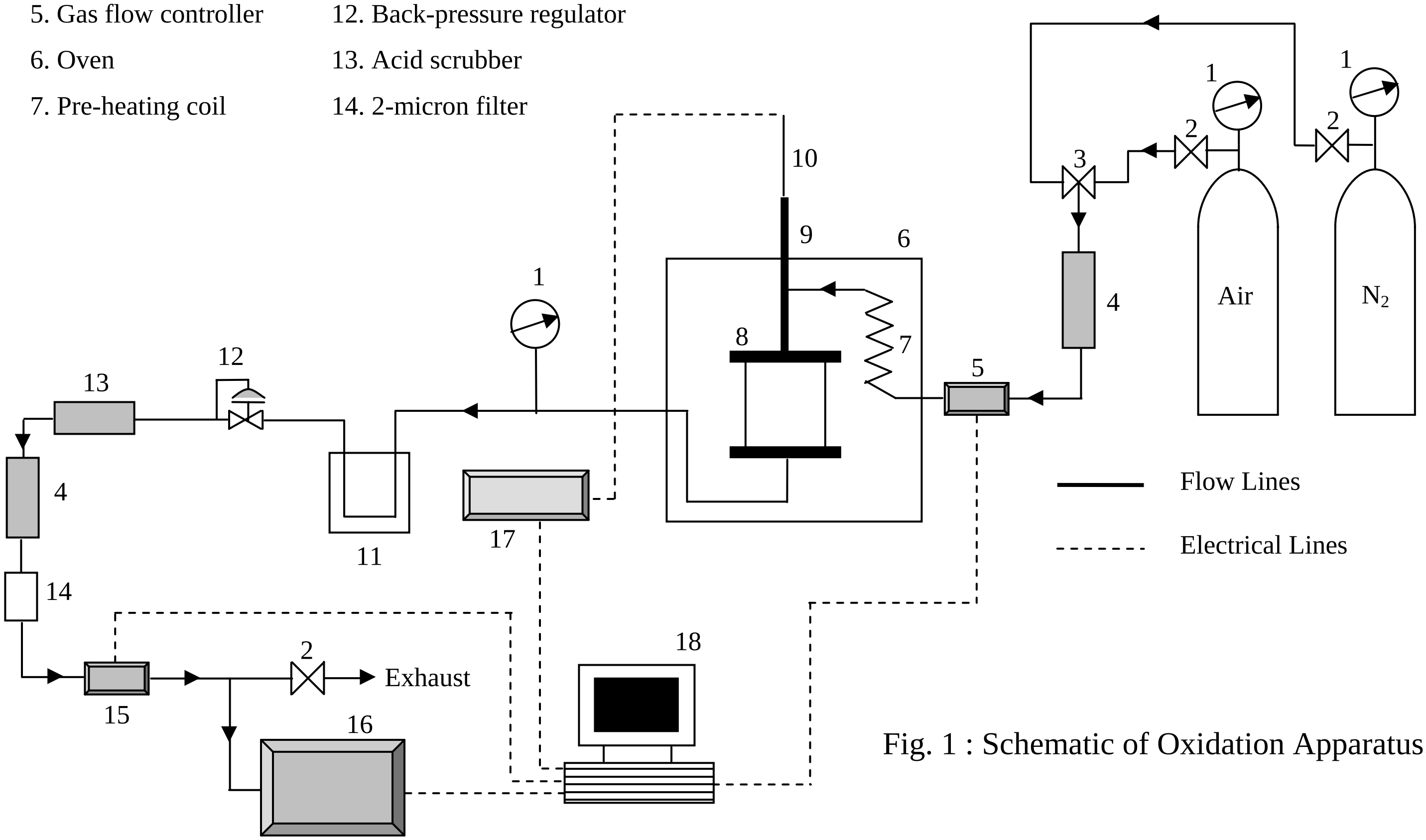

Fig. 1 : Schematic of Oxidation Apparatus.

when concentrations of carbon oxides in the effluent gas were down to trace levels. At this point, the residual mixture, which was invariably clean sand, was removed and weighed.

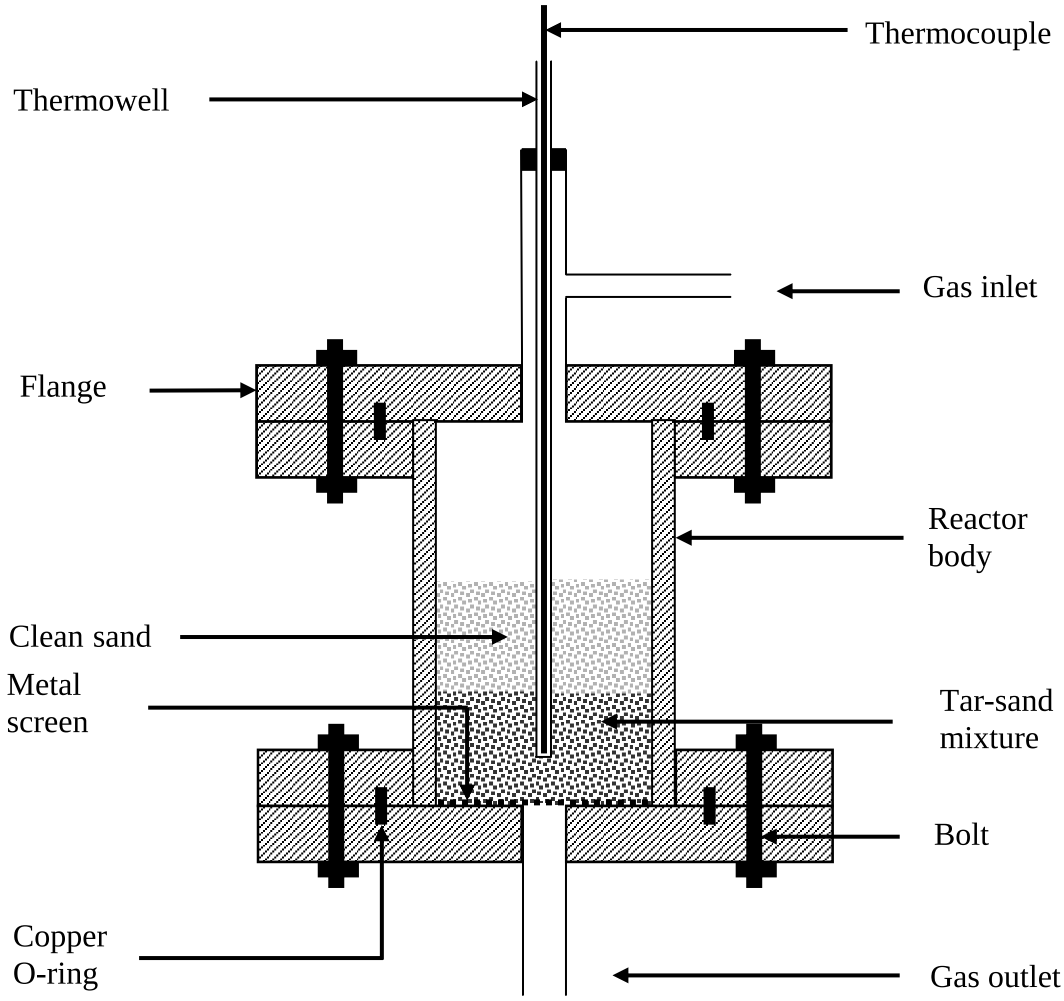

Fig. 2: Oxidation Reactor (not to scale).

RESULTS & DISCUSSION

Nine oxidation runs were conducted. Initial conditions and operating pressures for these runs are listed in Table 3.

Table 3: Initial Conditions and Operating Pressures of Oxidation Runs.

Run	Medium	Porosity (%)	Tar (g)	S_{oi} [*] (%)	Pressure (kPa)	Pressure (psia)
04	Sand	32.4	2.35	60.3	790.4	114.7
05	Sand	29.2	2.50	66.7	445.9	64.7
06	Sand	36.2	2.50	55.1	101.3	14.7
07	Sand	32.9	2.40	57.8	1169.4	169.7
08	Sand	30.5	2.44	49.6	1824.1	264.7
09	Sand	31.2	2.45	63.2	2513.2	364.7
10	Sand	32.2	2.40	63.4	3202.3	464.7
11	Core	34.3	2.28	52.6	790.4	114.7
12	Core	31.0	2.64	70.5	3202.3	464.7

[*] Initial tar saturation (percent of sand-pack pore volume).

Variations in effluent gas composition and temperature of the tar-sand mixture, both versus oxidation time, for Run 07 are shown in Fig. 3 to illustrate typical results. For comparison purposes, effluent gas composition (mol%) for a run was normalized by dividing each constituent’s concentration by the initial mass of tar for that run. Effluent gas composition of Fig. 3 reveals the two familiar oxidation peaks: a low-temperature oxidation (LTO) peak at about 325 ºC and a HTO peak at about 555 ºC. LTO of oil predominates normally below 350 ºC and produces mostly oxygenated hydrocarbons (alcohols, aldehydes, ketones, peroxides, and acids) with little carbon oxides (Fassihi et al., 1984, p. 399). Since HTO of the residual fuel was of more concern to this study, analysis and discussion will be focused on the HTO peak.

HTO-Peak Temperature

As shown in Fig. 4 for the sand runs (Run 04 to 10), the data indicates a clear shift in HTO peak towards lower temperatures with increase in pressure. Such trend is attributed to suppression of low-temperature evaporation of light hydrocarbons by higher pressures, which causes a larger fraction of these hydrocarbons to be available for HTO. The residual fuel would then be lighter and, thus, more reactive at lower temperatures.

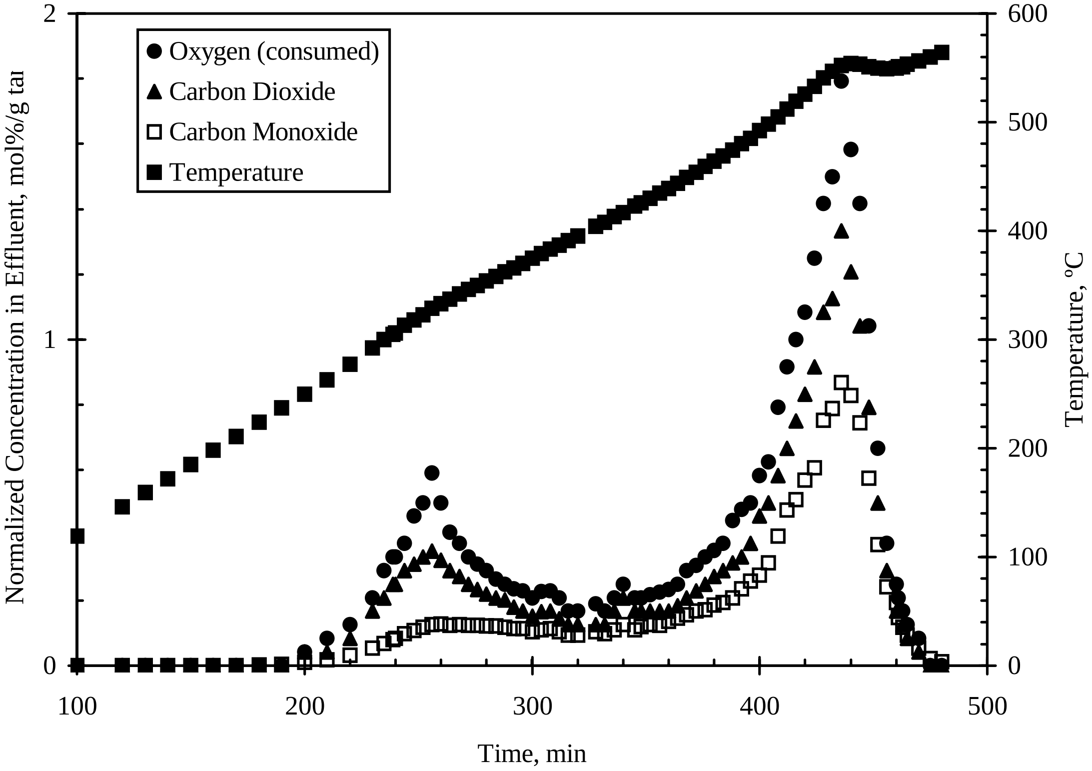

Fig. 3: Oxidation Data for Run 07.

The trend in HTO-peak temperature appears semi-logarithmic with pressure. Extrapolation to Arab-D reservoir pressure of 21 MPa (about 3000 psig) cannot be justified, however, without higher-pressure data. Nevertheless, HTO-peak temperature is expected to stay above 500 °C at that pressure, which is beyond normal in-situ combustion front temperatures. Shifted by 50 °C lower initially, LTO-peak temperature remained at about 325 °C with further increase in pressure as also shown in Fig. 4.

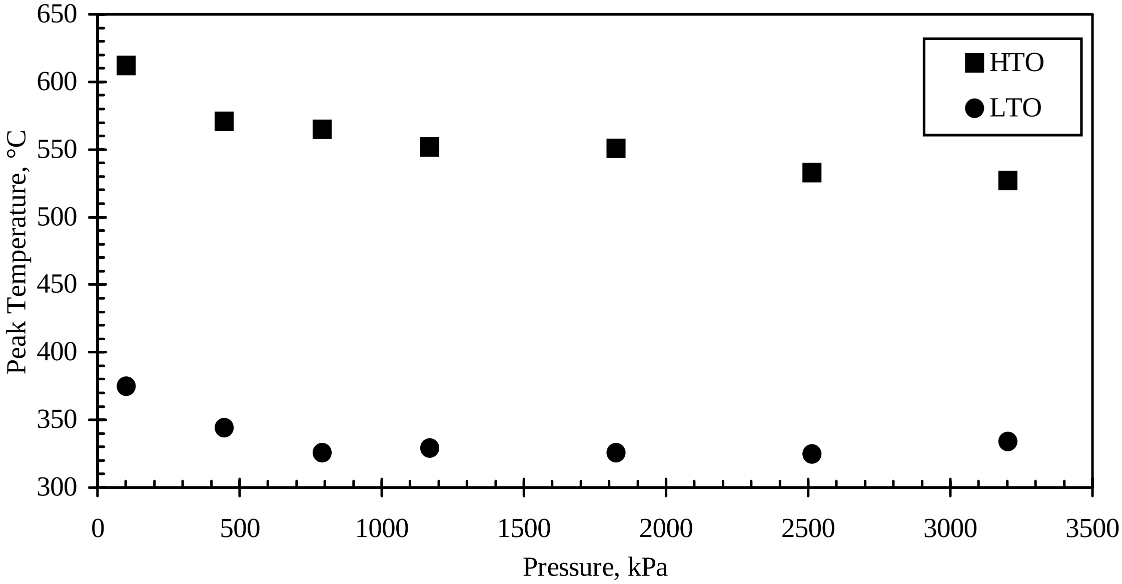

Fig. 4: Variation of Peak Temperatures with Pressure – Sand Runs.

Oxygen Consumption

The amount of O_2 consumed (normalized) at the HTO peak decreased steadily with increased pressure as shown in Fig. 5. It had been observed (Mamora, 1995) that oxygen bound to the oil by LTO was consumed later during HTO. As lighter hydrocarbons are generally more susceptible to LTO, the effect of pressure on evaporation described in the previous paragraph caused larger O_2 consumption at the LTO peak as also shown in Fig. 5. Then, oxygen bound by LTO compensated for later O_2 requirement, which explains the reduction in O_2 consumption observed during HTO.

Apparent H/C Ratio of Fuel

This ratio was computed by a stoichiometric balance on O_2 during HTO reaction assuming a) complete burning of the fuel as described by Equ. 1 and b) that oxygen unaccounted for in produced carbon oxides is consumed into water. Fig. 6

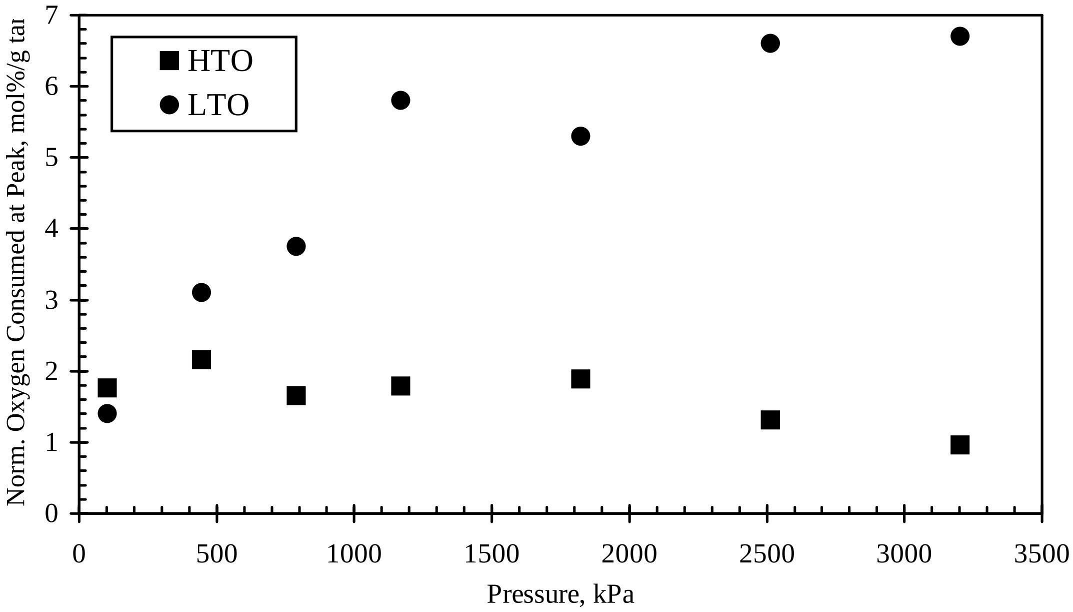

Fig. 5: Variation of Peak Oxygen Consumption with Pressure – Sand Runs.

shows a slight increase in the apparent H/C ratio of the fuel consumed at the HTO peak with increase in pressure for the sand runs. Given the large increase in O_2 consumption during LTO observed at higher pressures, and taking into consideration its effect on HTO consumption, increase in the true H/C ratio of the fuel with pressure should be much greater than what is shown by Fig. 6.

HTO Activation Energy

The graphical technique described in the literature (Fassihi et al., 1984, p. 408) was employed to estimate E_{HTO}. This technique is based on computing the relative rate of reaction, $R_{r,HTO}$ (min^{-1}), defined as

$$R_{r,HTO} = \Delta O_{2c} / \int_t^\infty \Delta O_{2c}\, dt \qquad (4)$$

Where ΔO_{2c} is oxygen consumed by HTO reaction (mol%) at a given time t (min). $R_{r,HTO}$ is related to the reaction's kinetic parameters by:

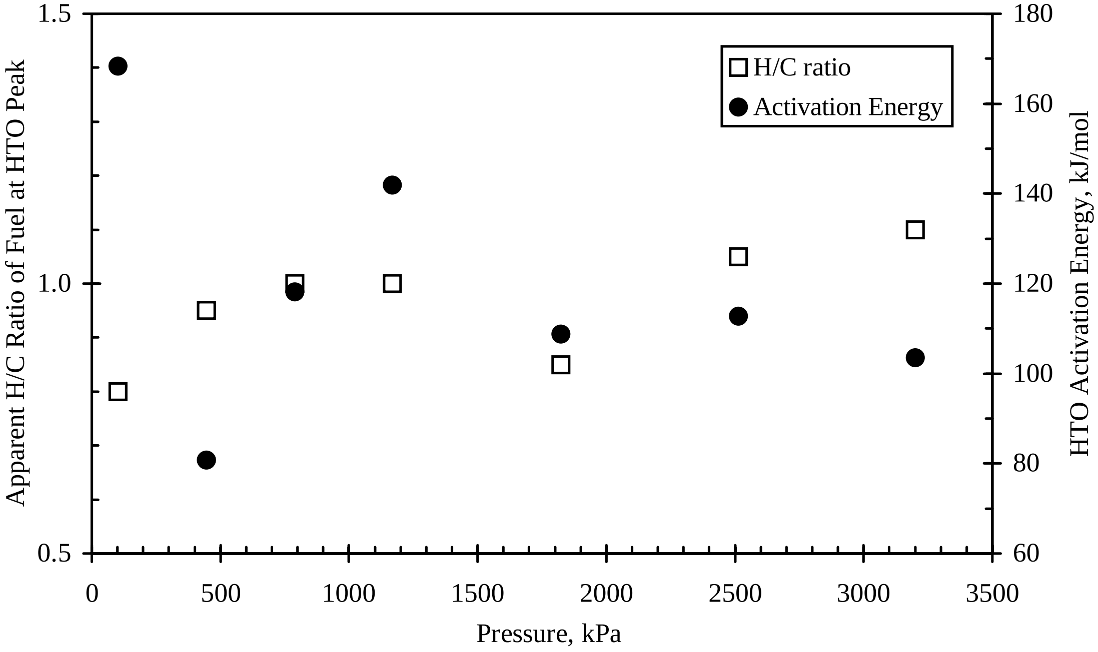

Fig. 6: Variation of Fuel Apparent H/C Ratio and HTO Activation Energy with Pressure – Sand Runs.

$$R_{r,HTO} = \beta \exp(-E_{HTO}/RT) \qquad (5)$$

Where β is a quantity involving experimental variables and other kinetic parameters, which are all constant for a given run. A semi-logarithmic plot of $R_{r,HTO}$ at a given time versus inverse of absolute temperature at that time should yield a straight line whose slope is $-2.303E_{HTO}/R$. The graphical technique is demonstrated in Fig. 7 for Run 07. Points selected for the straight-line fit correspond to O_2 consumption data on the low-temperature slope of the HTO peak. In that temperature range (T > 500 ºC), HTO is believed to be the only reaction within the sand and, with ample fuel, its rate is large enough to warrant accurate data. Beyond the HTO peak, fuel concentration becomes too low for meaningful rate values.

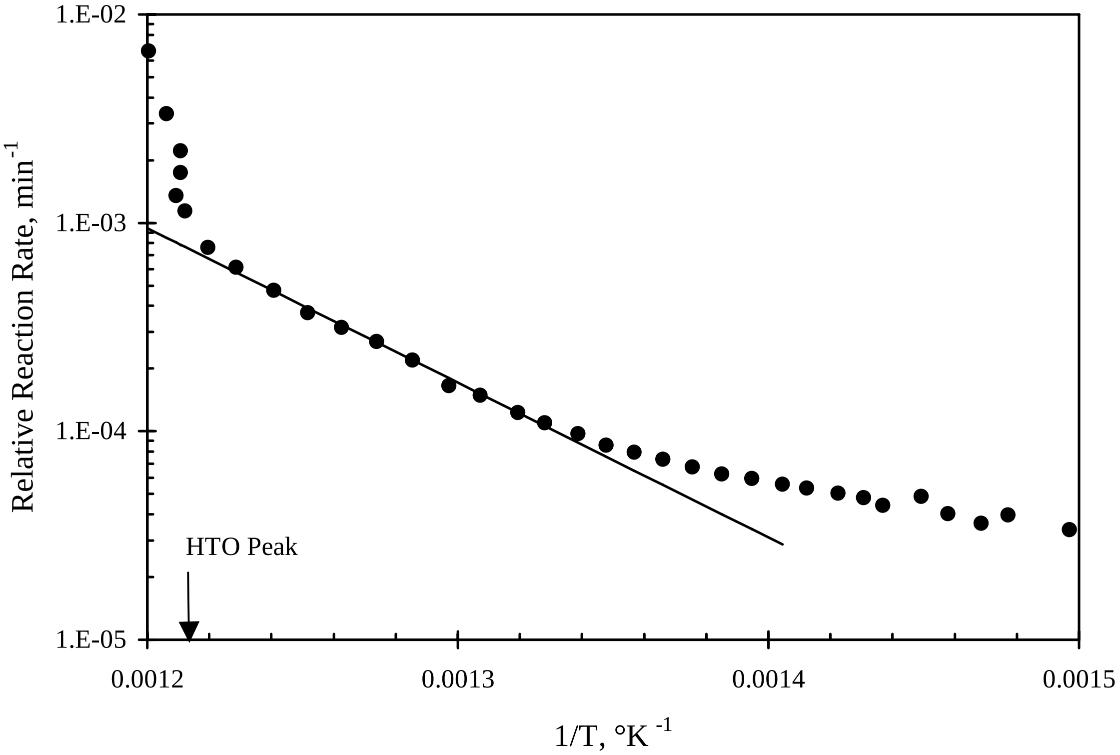

Fig. 7: Arrhenius Plot for HTO reaction – Run 07.

E_{HTO} data, also plotted in Fig. 6, shows clear decrease with increase in pressure. Once again, the lighter nature of the fuel is the cause of this trend. At Arab-D reservoir pressure, E_{HTO} is speculated to be above 80 kJ/mol. If true, this value is comparable to those measured for medium crudes at low pressures.

Effect of Porous Medium

Before conducting experiments with Arab-D cores, clean and dry samples were subjected to the same oxidation program to verify high-temperature stability of rock minerals (Calcite and Dolomite). No signs of chemical disintegration of rock were detected. Comparing the results of Runs 11 and 12 with Runs 04 and 10, respectively, revealed the following for the crushed-core runs:

(a) HTO peaks occurred at the same temperatures of equivalent sand runs and showed a similar effect of pressure.

(b) Compared with sand runs, normalized oxygen consumption at HTO peaks decreased while consumption at LTO peaks more than doubled. Such increase is attributed to larger unit surface area of the crushed cores rather than catalytic effects of rock minerals.

(c) Apparent H/C ratios of the fuel were comparable to the sand runs.

(d) E_{HTO} were about 18% higher than for corresponding sand runs, but showed the same trend with pressure.

The combination of high E_{HTO} and high HTO-peak temperature for the crushed cores render the possibility of sustained in-situ combustion through the tarmat of Arab-D reservoir rather questionable. To test this hypothesis, combustion-tube experiments on the tar are underway and their results will be reported shortly.

CONCLUSIONS

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

(1) A tar with physical and chemical characteristics similar to those of a Saudi Arabian reservoir tar was prepared from the reservoir's crude.

(2) The tar showed oxidation characteristics typical to heavy crude oils.

(3) HTO-peak temperature decreased with increase in pressure but remained above 500 ºC.

(4) Oxygen consumption at HTO peak decreased with pressure as a result of increased Oxygen uptake during LTO.

(5) Apparent H/C ratio of the fuel showed an average value of 1 with a slight increase with pressure. True H/C ratio is expected to be much larger, especially at higher pressures.

(6) HTO activation energy showed marked decrease with increase in pressure.

(7) Natural carbonate-core material affected oxidation kinetics only through its larger surface area. HTO activation energy was significantly larger.

(8) It appears that the effect of pressure on oxidation kinetics of tar is primarily through suppression of light-end evaporation at low temperatures.

(9) The tested tar appears to be incapable of sustaining in-situ combustion in loose sand or crushed reservoir-core material under the applied experimental conditions.

ACKNOWLEGEMENT

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