CSCanada
Advances in Petroleum Exploration and Development
Vol. 4, No. 2, 2012, pp. 58-62
DOI:10.3968/j.aped.1925543820120402.792

ISSN 1925-542X [Print]
ISSN 1925-5438 [Online]
www.cscanada.net
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Low Temperature Oxidation Experiments and Kinetics Model of Heavy Oil

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Received 25 September 2012; accepted 5 December 2012

Abstract
Air injection is an effective technique for improved oil recovery. For a typical heavy oil sample, the effects of temperature on the oxidation characteristics were studied by low temperature oxidation (LTO) experiments. Kinetic parameters such as activation energy, frequency factor (pre-exponential factor) and reaction order are determined by using Arrhenius Equation. These parameters provide a theoretical basis for numerical simulation of LTO taking place during air injection in heavy oil reservoirs. The results of LTO experiments show that heavy oil has good low temperature oxidation properties and LTO reaction rate is mainly related to temperature, oxygen partial pressure and properties of crude oil. In the experimental temperature range, the oxidation reaction can effectively consume oxygen and at the same time produce large amount of CO_2.

Key words: Air injection; Low temperature oxidation; Kinetics model (70-150 °C)

Chen, Z.Y., Wang, L., Tang, L.Z., & Huang, A.Y. (2012). Low Temperature Oxidation Experiments and Kinetics Model of Heavy Oil. *Advances in Petroleum Exploration and Development*, *4*(2), 58-62. Available from: http://www.cscanada.net/index.php/aped/article/view/j.aped.1925543820120402.792
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INTRODUCTION
Air injection is an effective technique for improved oil recovery (Greaves *et al*., 2000; Greaves *et al*., 1999). Air injection process has been proven to be an effective improved oil recovery technique, which is typically suitable as a secondary oil recovery method for deep reservoirs with very low permeability and poor water injectivity (Yu *et al*., 2008; Yu & Yang *et al*., 2008; Zhao *et al*., 2005). Air injection is currently considered by many operators for a better recovery.

The reactions of hydrocarbon with oxygen in an oil reservoir can be classified into low temperature oxidation and high temperature oxidation (HTO, also known as in-situ combustion.) (Adegbesan *et al*., 1984; Babu & Cormack, 1983). Traditionally, air injection is applied to heavy oil reservoirs via an in situ combustion process (HTO), and oil recovery is enhanced mainly because of steam flooding and viscosity reduction caused by the heat generated in the oxidation reaction at high temperatures. Nowadays, air is also injected into light oil reservoirs. In deep, heavy oil reservoirs, original temperatures are relatively high compared with those light oil reservoirs, thus the oil components are more reactive with oxygen, making it possible for the LTO process to take place spontaneously at reservoir temperatures (Ren *et al*., 1999). During air injection process, a possibility exists that LTO process happens in heavy oil reservoirs may develop into an HTO one, which could make it less trouble during in-situ combustion, because there is no need for the oil to be ignited to get the combustion started. The LTO reaction consumes oxygen in the injected air and produces flue gas (mainly contains N_2, CO_2, and light hydrocarbons) to displace oil, and the thermal effect generated from the reaction can be a bonus for oil recovery (Yu *et al*., 2009; Zhang *et al*., 2006).

Air injection techniques have been used in many field projects for IOR. Field tests have been conducted in a few heavy oil reservoirs in China in recent years, including Liaohe oilfield and Henan oilfield. Results from Liaohe oilfield have shown significant benefits from air injection via the LTO process (Chen *et al*., 2012). Up to now, 2-3% oil production has been achieved by air injection in the pilot region during 2 years of air injection.

According to the experience gained in field projects and laboratory studies, the following arguments are made in favor of the air injection process for heavy oil reservoirs (Chen & Zhang *et al*., 2012). Air is universally abundant, and hence does not pose any supply constraints. It may have significant cost benefits as an alternative to other gas injectants such as CO_2 and N_2. It appears technically and economically successful in all projects to date. There are also concerns on safety and corrosion issues which are the main reasons why air injection has not been well accepted in the industry. The risk of potential explosion because of oxygen breakthrough in producers is the major concern, which is particularly important during air injection LTO operations. Thus, the oxygen consumption or oxidation rate in heavy oil reservoirs is one of the key factors for reservoir selection and evaluation, as well as for the project design. These must be taken seriously in the design and implementation of air injection projects.

It is essential to establish reliable reaction models and obtain corresponding kinetic parameters in order to understand the LTO mechanisms and conduct reservoir simulation for air injection process. In this study, typical light and heavy oil samples were used to study the LTO reaction process with a small-batch reactor (SBR). Effects of temperature on the oxidation rate of heavy oil samples were also investigated. An improved reaction model is presented based on LTO reaction mechanisms of heavy oils. The kinetic parameters, in terms of the Arrhenius activation energy and reaction frequency factor, were obtained from the results of SBR experiments.

1. HEAVY OIL STATIC OXIDATION EXPERIMENTS

1.1 Materials

A heavy crude oil sample from the Henan oilfield in China was selected for experiments in this study. The viscosity of the oil is of 50719.6 mPa·s at reservoir conditions (31 °C and 3.9 MPa), and its density is 0.963 g/cm^3 (at standard surface conditions). Crushed reservoir cores and washed quartz sands were used to prepare oil sand samples. Brine water with a salinity of 20 mg/L was reconstituted according to the composition of the reservoir aquifer.

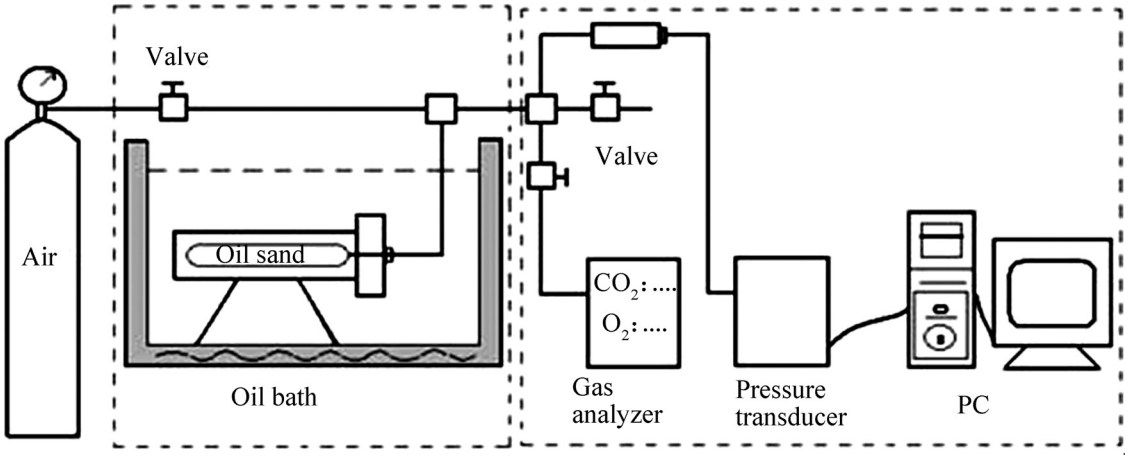

Figure 1
High Pressure and Constant Temperature Static Oxidation Equipment

1.2 Heavy Oil-Air Static Oxidation Experiments

A SBR (100 mL in volume) was used to perform the LTO experiments at static conditions (see Figure 1). 60 mL of oil or oil-sand mixture was loaded into the reactor, leaving the rest of the space for air to be then charged to the required pressure. During the experiment, pressure and temperature profiles were recorded. Normally, a reduction of pressure was observed, which is due to oxygen consumption.

1.3 Results and Discussion

It can be seen from Figure 2 and Figure 3 that during the experiment, oxygen was consumed, and there is a reduction of pressure. The LTO reaction rates (oxygen consumption rates) at different temperatures were calculated. It has been observed that, temperature is an important factor of oxidation reaction. It is interesting to note that the reaction rate of heavy oil increased rapidly as the temperature was raised from 100 °C to 120 °C.

Figure 3 shows the pressure drop curves of heavy oil and light oil samples for the LTO reaction at 70 °C. The experimental results in Figure 3 indicate that heavy oil can be more easily oxidized than light oil at low temperature. Noteworthy, the heavy oil sample exhibited a higher oxidation activity (higher oxygen consumption rate) than the light oil during the LTO process.

During the experiments, the reaction is considered ended when no further pressure reduction was observed. To maintain the pressure in the reactor, the compositions of the produced gas were only measured after the reaction came to an end. Table 1 shows the measured results of O_2 and CO_2 from the LTO experiments. As it is indicated in Table 1, at higher temperatures, more CO_2 was produced.

Table 1
Experimental Results of a Heavy Oil Sample at LTO Conditions

T/°C	Reaction time/h	CO_2 produced/%	O_2 after reaction/%	LTO reaction rates 10^{-5}mol/(h·mL)
70	143	1.9	9.8	1.108
90	55	3.6	1.9	3.75
100	32	5.2	1.2	4.92
120	18	7.8	1.1	6.52

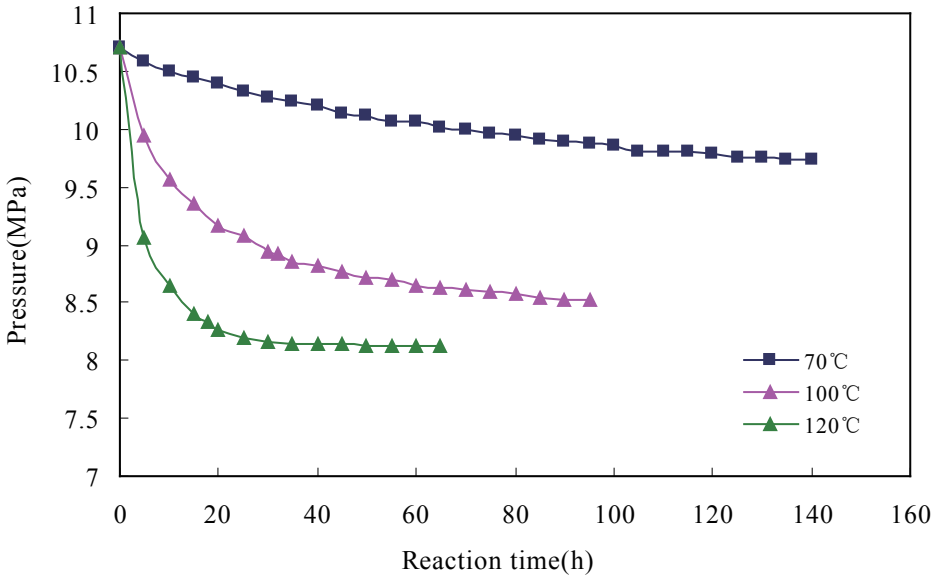

Figure 2
The Influence of Temperature on Oxidation Reaction

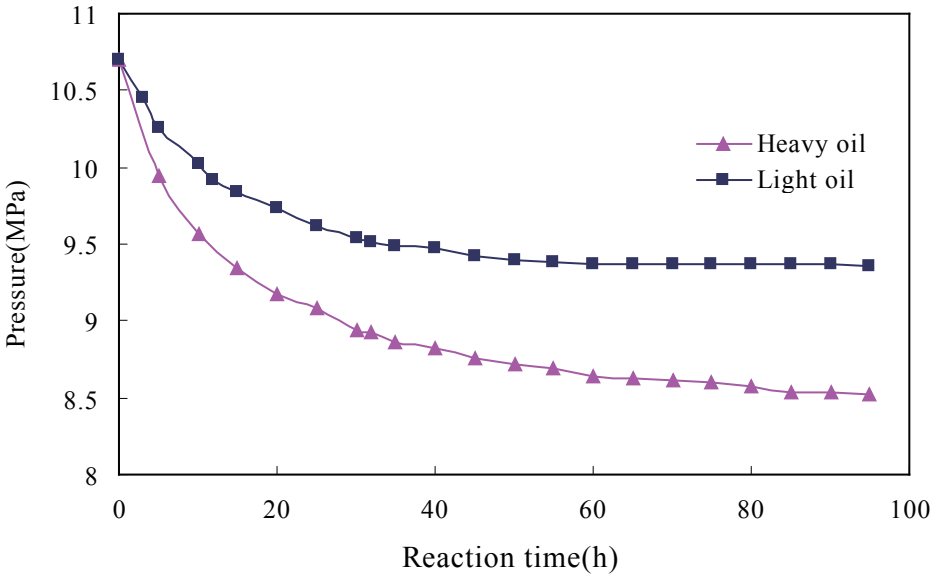

Figure 3
Comparison of Oxidation Rate for Heavy and Light Oils (100 °C)

2. LOW TEMPERATURE OXIDATION KINETICS MODEL

The LTO reaction consumes oxygen in the injected air and produces flue gas (mainly contains N_2, CO_2, and light hydrocarbons) to displace oil, and the thermal effect results from the reaction can be a bonus for oil recovery. The low temperature oxidation is a complex process, because it contains a series of reactions. In order to simplify the simulation, it is assumed that only

heavy components (C_{10+}) in the oil phase took part in low temperature oxidation reaction. The crude oil low temperature oxidation reaction equation is as follows:

$$C_{10+} + 1.5O_2 \rightarrow 0.8661C_{10+}O + CO_2 + H_2O$$

This reaction model is obtained by analyzing the gas composition of the produced gas of LTO experiments, taking into consideration the dissolving of O_2 and CO_2 in the liquid phase. According to the calculation results, the ratio between the amount of the consumed O_2 and the produced CO_2 is approximately 1.5, so the stoichiometry is 1.5.

Low temperature oxidation reaction rate is a function of temperature, oxygen partial pressure and the concentration of crude oil. It can be depicted by Arrhenius equation:

$$v = \frac{dp_x}{dt} = k_0 e^{-E/RT} [p_x]^m \left[C_{10}^+\right]^n$$

Where, v is LTO reaction rate, kPa/s; $[P_x]$ is oxygen partial pressure, kPa; t is time, s; k_0 is pre-power law index, L/(s·kPa); E is activation energy, J/mol; R is universal gas constant, 8.314 kPa·m^3/ (kmol·K); T is temperature, K; m is reaction order of oxygen partial pressure; n is reaction order of crude oil concentration.

k_0, E, m and n are the so-called reaction kinetics parameters, which are relevant to oil and reservoir rock properties, and can be derived from experimental results.

Usually, when there is no mass transfer limitation, oil oxidation can be assumed as a first order reaction (m = 1 and n = 1) with respect to oil concentration and oxygen partial pressure. This is also required for modeling the oxidation reaction in reservoir simulation in order to maintain material balance in case where oil and oxygen were completely consumed in some area.

However, in order to derive the activation energy E from the SBR experiments, the above model needs to be simplified. Because the reaction rate is very low at low temperatures and it is independent of oxygen partial pressure, so m can be assumed to be zero. Since the oil loaded in the reactor is greatly in excess compared with the limited amount of oxygen, n is also zero. The model is simplified as:

$$v = \frac{dp_x}{dt} = k_0 e^{-E/RT}$$

Logarithm on both sides:

$$\ln v = \ln k_0 - \frac{E}{R} \times \frac{1}{T}$$

A linear relationship can be found between the logarithm of the reaction rate ($\ln k_0$) and the reciprocal of the absolute temperature ($\frac{1}{T}$). The reaction rate can be calculated from the measured rate of the decrease in the total pressure in the reactor, and is a function of the absolute temperature only. The parameters $\ln k_0$ and $-\frac{E}{R}$ can be obtained by curve fitting of the experimental data at different temperatures as shown in Figure 4.

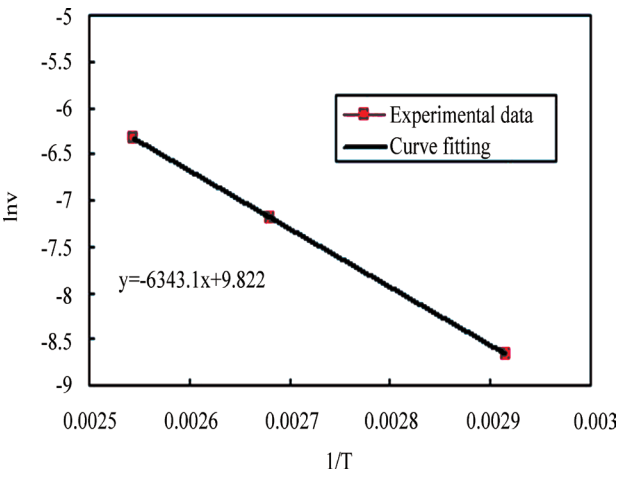

Figure 4
Rate Constant Versus Temperature (1/T)

According to heavy oil LTO experiments results, it is calculated that, E is 52736.32 J/mol, pre-power law index k_0 is 18435.6 L/(s·kPa). For reservoir simulation studies, reaction constant k_0 and activation energy E can be adjusted based on the results of oxidation tube experiments and field data.

CONCLUSIONS

LTO can occur spontaneously at typical reservoir temperatures after air is injected into heavy oil reservoirs during IOR processes, in which oxygen is consumed and CO_2 is produced as partial reaction products. In this study, different oil samples were used to reveal the reactivity of different oil samples in terms of LTO reactions, and the following conclusions can be drawn:

(1) Air injection has other gas (N_2 Flue gas CO_2) injection's advantages and additional thermal effect to increase oil recovery.

(2) Typical heavy oil samples used in the experiments have good LTO reactivity. In the reservoir conditions it has higher rate of oxidation and can effectively consume oxygen and produce large amounts of CO_2. Heavy oil has better oxidation activity than light oil.

(3) According to the results of heavy oil-air oxidation experiments at different temperatures, and based on the Arrhenius equation, we can get that the activation energy of the oxidation reaction of the oil sample used is 52736.32 J/mol, and the frequency factor is 180435.6 L/(s·kPa) and the reaction enthalpy is 457.2 KJ/mol.

ACKNOWLEDGEMENTS

The authors would like to thank Sinopec for financial support of this research work and the permission to publish this paper. The assistance of Miss. Tang lingzhi in experimental work is also greatly appreciated.

REFERENCES

[1] Greaves, M., Ren, S. R., & Rathbone, R. R., *et al*. (2000). Improved Residual Light Oil Recovery by Air Injection (LTO Process). *Journal of Canadian Petroleum Technology*, *39*(1), 57-61.

[2] Greaves, M., Ren, S.R., & Xia, T.X. (1999). New Air Injection Technology for IOR Operations in Light and Heavy Oil Reservoirs. *SPE Asia Pacific Improved Oil Recovery Conference*, 25-26 October 1999, Kuala Lumpur, Malaysia.

[3] Yu, H.M., Ren, S.R., & Wang, J. X., *et al*. (2008). Numerical Simulation Study on Enhanced Oil Recovery by Air Injection Process in Shengli Oilfield. *Oil Drilling & Production Technology*, *30*(3), 105-109.

[4] Yu, H.M., Yang, B.Q., & Xu, G.R., *et al*. (2008). Air Foam Injection for IOR: From Laboratory to Field Implementation in Zhongyuan Oilfield China. *SPE/DOE Symposium on Improved Oil Recovery*, 20-23 April 2008, Tulsa, Oklahoma, USA.

[5] Zhao, B., Gao, H.T., & Yang, W.D. (2005). Potentials of Improved Oil Recovery by Air Injection in Zhongyuan Oilfield. *Oil-Gasfield Surface Engineering*, *24*(5), 22-23.

[6] Adegbesan, K. O., Donnelly, J. K., & Moore, R. G., *et al*. (1984). LTO Kinetic Parameters for In-Situ Combustion: Numerical Simulation. *SPE Res*., *2*(4), 573-582.

[7] Babu, D. R., & Cormack, D. E. (1983). Low Temperature Oxidation of Athabasca Bitumen. *Can. J. Chem*., *61*, 575-580.

[8] Ren, S. R., Greaves, M., & Rathbone, R. R. (1999). Oxidation Kinetics of North Sea Light Crude Oils at Reservoir Temperature. *Chemical Engineering Research and Design*, *77*(A5), 385-394.

[9] Yu, H.M., Ren, S.R., Zuo, J.L., & Wang, R.H. *et al*. (2009). Experiment of Improved Oil Recovery by Air Foam Injection Low Temperature Oxidation Process. *Journal of China University of Petroleum*, *33*(2), 94-98.

[10] Zhang, X.B. (2006). Applied Research of Steam-Carbon Dioxide-Auxiliary Agent Huff and Puff Technology. *Acta Petrolei Sinica*, *27*(2), 80-84.

[11] Chen, Z.Y., Yu, H.M., Zhang, F., & Ren, S.R. (2012). Low Temperature Oxidation Kinetics Model and Analysis of Influence Factors in Air Foam Flooding of M15 Block. *Science Technology and Engineering*, *18*(12), 4364-4367.

[12] Chen, Z.Y., Zhang, F., & Ren, S.R. *et al*. (2012). Crude Oil Phase Behavior and Its Influence Analysis by Air Injection. *Applied Chemical Industry*, *41*(7), 1147-1154.