In-situ heavy oil upgrading by high temperature oxidation through air injection

Xiaodong Tang[1], Wanfen Pu[1a*], Yu Yang[2], Renbao Liu[1]

[1]State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu, Sichuan 610500, China;

[2]Southern Sichuan Gas Mine of PetroChina Southwest Oil and Gas Field Company, Chengdu, Sichuan 642300, China

Abstract: Air injection has been widely considered as a technology to enhanced heavy oil recovery on account of the heavy oil upgrading caused by high temperature oxidation during this process. This paper aims at exploring the effects of oxidation thermal processing in a porous media at high temperature from 500 to 540°C which is the high temperature oxidation range of heavy oil known from TG results, and reaction time from 8 to 16 hours for heavy oil upgrading. It was suggested that the viscosity decreased with the temperature and retention time increased due to getting less ring structure seen from IR Spectrum results. It was observed that the viscosity of heavy oil was reduced 1 to 2 orders of magnitude. Besides, the kinetics of heavy oil upgrading were analysed using five pseudo components including HO (C_{35+}), MO ($C_{15} \sim C_{35}$), LO ($C_5 \sim C_{14}$), coke, G (gas products) and successfully predicted the products results with an error of 4.34%, and great correlation to Arrhenius equation. The activation energies obtained are in the range of $44 \sim 215$ kJ/mol. This work has great value in revealing the mechanisms of high temperature oxidation heavy oil upgrading and assisting heavy oil production.

1. Introduction

Heavy oil as an unconventional resource is much more conventional light oil [1]. With the increase of energy requirement and the decrease of conventional energy, it is essential to increase the heavy oil production. The viscosity of heavy oil is thoroughly sensitive to temperature. Air injection has been extensively considered as a great technology to enhanced heavy oil recovery due to the high temperature caused by oxidation, resulting in the decrease of heavy oil viscosity [2-5]. As most scholars agreed, there are low temperature oxidation (LTO) and high temperature oxidation (HTO) during the process of air injection [6, 7]. LTO is always considered to increase the viscosity of crude oil due to polymerization [8], but HTO can decreased the viscosity on account of the destroyed structure under high temperature of resins and asphaltenes which is the main contribution of viscosity.

The thermal analysis methods including thermogravimetry (TG), differential scanning calorimeter (DSC), and accelerating rate calorimeter (ARC) were used to study the oxidation behaviors of heavy oil [2, 9, 10]. However, the experimental ways above cannot obtain the produced samples for upgrading analysis owing to the tested little oil. Then, the TG-MS and TG-FTIR technologies which could get the production gases information including type and fraction, are used to study the oxidation process of heavy oil. Kök et al [11] used TG-MS to explore the crude oil oxidation behaviors and found that the generation gases composed of hydrogen, carbon dioxide, carbon monoxide, sulfur oxides, low carbon hydrocarbon gas, and etc. Zhao et al [6] investigated the oxidation characteristics of heavy oil and its SARA fractions by TG-FTIR, and reported that in addition to carbon oxides and hydrocarbon gases, there is also water. Nevertheless, the liquid and solid products still cannot be analyzed. Hence, the larger high-temperature and high-pressure reactors were used to investigate the variation of physicochemical properties of crude oil after oxidation. Pu et al [1, 8] found that the viscosity of oil increased during LTO process and there are coke and gases generation during oxidation process. Sadikov et al [12] studied the HTO (combustion) using combustion tube, and reported that the viscosity decreased from 2073.36 mPa·s to 43.18 mPa·s. Yang et al [13] evaluated the upgrading of bitumen through co-injection of steam and oxygen, and pointed that the bitumen upgraded significantly at a temperature of 430°C which can result in the upgrading of heavy oil. Hosseinpour et al [14] investigated the heavy oil upgrading under the condition of supercritical water with a temperature from 400 to 500°C, and suggested that the more obvious upgrading could be obtained by greater water.

a*puwanfen@126.com

In summary, heavy oil could be upgraded by HTO. The physicochemical properties and kinetics of heavy oil upgrading which is vital for the mechanism of heavy oil upgrading are rarely studied in higher temperature. In this work, the changes of heavy oil structure and components after HTO are focused on. Besides, the kinetics are also researched according to the products of heavy oil upgrading. We believe that the research results could provide some parameters for upgrading during air injection.

2. Materials and methods

2.1 Materials

The properties of heavy oil obtained from Xinjiang oil field were shown in Table 1. The SARA components including saturates (S), aromatics (A), resins (R), and asphaltenes (A) of heavy oil were separated using the industrial standard method of China Petroleum NB/SH/T 0509-2010. The porous medium was made from the broken debris with 40~80 mesh got from oil field.

**Table 1. The properties of heavy oil.**

Viscosity at 50°C ($mPa \cdot s$)	Density at 20°C (g/cm^3)	Water cut (%)	SARA components (wt%)				Element analysis (wt%)				
			S	A	R	A	C	H	O	N	S
15682	0.946	10.2	10.25	21.75	24.41	44.59	78.21	10.26	6.35	1.09	3.82

2.2 Methods

TG was brought from NETZSCH, Germany. For the test, approximately 5 mg of sample was weighed and placed in the alumina crucible. The flow rate of air with 99.99% high purity was 50 mL/min for bringing the production gases out. The heating rate was 15K/min.

The experimental instrument composed of air bottle, gas flowmeter, valve, pressure sensor, reactor, and gas liquid separator, was shown in Figure 1. The reactor with a maximum temperature 600°C and a maximum pressure 40MPa can be self-heated by energized coil. The gas flowmeter with a maximum pressure 70MPa was purchased from Bronkhorst, Netherlands.

The sample is a mixture consists of debris and heavy oil, and the debris/oil volume ratio is 3:1. The mixture with 60 mL was first placed in the reactor, then the air was injected into the container at 250 mL/min flow rate until the air/oil volume ratio reached 900:1. The mixture reacted under the temperature from 500 °C to 540°C, and the residence time was from 4h to 16h. After that, the products were separated by gas liquid separator, the composition of liquid product was analysed using GC (Agilent 7890B, USA) and GC-MS (Aglient 7890A-5975C, USA) for getting the carbon number distribution, and FTIR with scanning wavelength range from 500 to 4000 cm^{-1} (Thermo Scientific Nicolet 6700, USA), the absolute volume of gas product was metered by gas flowmeter, and the gas composition was detected through GC (Agilent 7890B, USA).
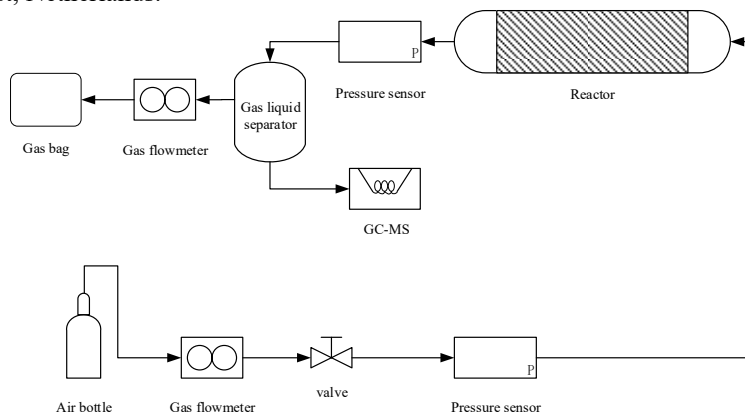

Figure 1. The experimental flow chart.

3. Results and discussion

3.1 TG analysis

Figure 2 shows the TG and DTG results of the heavy oil. There are for stages of weight loss in the oxidation process. With the temperature increasement, the weight started to decrease, the 12.5% weight reduction at the temperature of 109 ℃ whereas the water cut is 10.5%. It indicated that there are also light components evaporated in this temperature range. Then, the C-H bond would be destroyed by O atom and the carbon and oxygen would combine to form various partial oxides. It should be pointed out that these oxides can deteriorate the oil with a higher viscosity in view of the air injection process. Next,

a range of dehydrogenation, poly-condensation, and aromatization reactions for fuel deposition which can provide the raw materials for HTO are involved in FD [2]. Last, the activated fuel including heavy components would occur strong oxidation and combustion reactions, resulting in the decrease of viscosity. Therefore, the HTO of this heavy oil at the temperature from 490 °C to 590 °C, with some contributions to heavy oil upgrading was chosen as the experimental conditions.
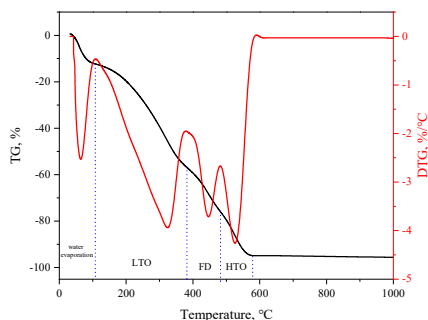
**Figure 2.** The TG and DTG results of heavy oil.

3.2 Products analysis

The changes of viscosity of heavy oil under different conditions were performed in Figure 3. With the temperature and retention time increase, the viscosity of heavy oil got lower. It is ascribed to two factors. The one is that higher temperature with higher energy can easier destroy the structure of asphaltenes which is the main reason for higher viscosity. The other is that more heavy components would be oxidized at longer time. The result presented a linear relationship between the logarithm of viscosity and reaction time, and the slope increased as the temperature increased, meaning keeping a higher combustion temperature is an excellent way for heavy oil upgrading during air injection process. Besides, there are also gases and coke generation which was also found in previous study [1].
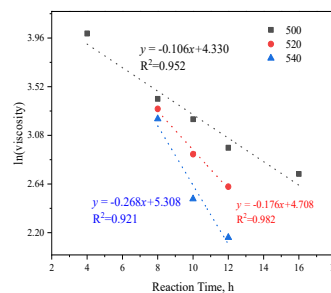

Figure 3. The variation of heavy oil viscosity at different temperature and different reaction time

The infrared spectrum detected results of heavy oil under different temperature were exhibited in Figure 4. The original state of oil was expressed in Figure 4 (a), and it was observed that O-H, C-H, and N-H, which are general in oil. Besides, the P-H represented that there are benzene rings, which are usually in the structure of resins and asphaltenes. The oil after the HTO reaction under 500°C and 10 hours was detected and plotted in Figure 4 (b). It was found that the transmittance increase of P-H and transmittance decrease of O-H and N-H, meaning the content decrease of P-H content increase of O-H and N-H according Lambert-Beer's law. It should be mentioned that the increase of Ⅰ area should be caused by the increase of O-H rather than N-H. The crude oil would become alcohols, aldehydes, acids and finally carbon dioxide during oxidation process [15], which the reason of the increase of O-H. And there is no way for the generation of N-H. The upgrading oil occurred oxidation reaction under the temperatures of 500°C and 540°C, the time of 10 hours, were respectively performed in Figure 4 (c) and (d). It was suggested that the less P-H and more C-H due to alcohols further oxidized to carbon oxides. Moreover, there is even no P-H in oil oxidized at 540°C, further verified that the lower viscosity was caused the aromatic ring structure. Therefore, the temperature is crucial to heavy oil upgrading.
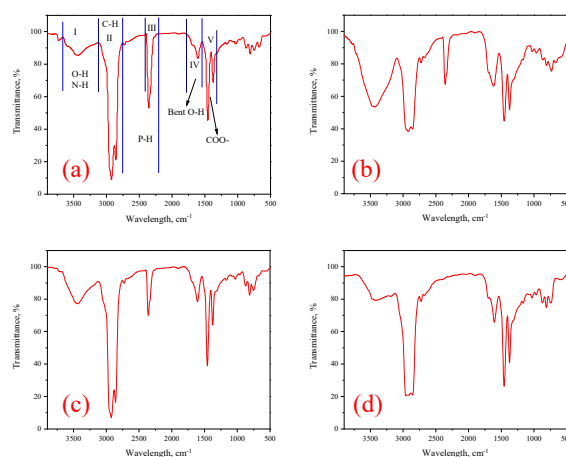
Figure 4. The infrared spectrum results of heavy oil, (a) original, (b) 500°C reacted 10 h, (c) 520°C reacted 10 h, (d) 540°C reacted 10 h.

The GC-MS result of crude oil oxidized at 540°C and 10 hours was shown in Figure 5. It was founded that there is no aromatic ring structure due to the high temperature oxidation, which is consistent with the infrared spectrum results. A various of alkanes were detected, indicating that alkanes are the more stable structure, because resins and asphaltenes always have unstable structures such as N-H and S-H. Therefore, it may be an advisable method to retain a higher combustion temperature in air injection for better upgrading. In addition, the water has been proved favorable influence on heavy oil upgrading [14], so air injection applied the heavy oil reservoirs adopted steam drive or steam assisted gravity drainage may get greater results[5].
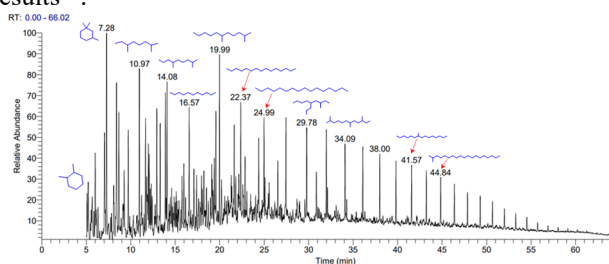
Figure 5. The GC-MS result of oil oxidized at 540°C and 10 hours.

3.3 Kinetics

The lumping technique including the definition of pseudo components and pseudo reactions simplified the problem from a mathematical perspective was always employed for the kinetic model of heavy oil due to the complexity of its composition and the difficulty of establishing the model containing a large number of chemical components related to each other.

In this paper, the kinetic model composed of 5 pseudo components comprising 9 reactions was used. Figure 6 presents the reaction scheme proposed of the kinetic model. The kinetic model consists in 5 lumps including HO (heavy components, C_{35+}), MO (medium components, C_{15}-C_{35}), LO (light components, C_5-C_{14}), coke, and G (gas), which are common in crude oil oxidation. Each of the 9 reactions is expressed as the kinetic equation (R_j) which is a functions of mass percentage (wt%), composition (y_j) and reaction rate (k_i).

It is assumed that all reactions are irreversible and first-order, the reaction rate of each lump is given by the following equation:

HO: $\quad R_{HO} = -(k_1 + k_2 + k_3 + k_4)y_{HO}$

MO: $\quad R_{MO} = k_1 y_{HO} - (k_5 + k_6 + k_7)y_{MO}$

LO: $\quad R_{LO} = k_2 y_{HO} + k_5 y_{MO} - (k_8 + k_9)y_{LO}$

coke: $\quad R_{coke} = k_3 y_{HO} + k_6 y_{MO} + k_8 y_{LO}$

G: $\quad R_G = k_4 y_{HO} + k_7 y_{MO} + k_9 y_{LO}$

Where R_j is the reaction rate of j component (wt%/h), k_i is the reaction rate constant (1/h), y_j is the j component mass fraction (%).
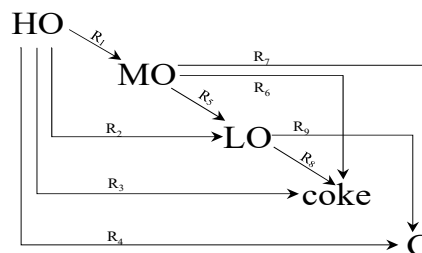
**Figure 6.** The proposed kinetic model for heavy oil upgrading by HTO.

The composition of products at different temperature and different reaction time was used to calculate the kinetic parameters. The relationship between reaction rate constant and temperature requires to follow the Arrhenius law, which is a limit of the model. Based on data fitting, the apparent activation energy E_a and apparent preexponential factor A for reactions were calculated by the followed equation.

$$lnk = lnA - \frac{E_a}{RT} \qquad (1)$$

Where, k is a rate constant, A is a pre-exponential factor, E_a is a reaction activation energy, and R is the gas constant.

The model was solved by least square method (with the minimum sum of squares of errors as the target) in MATLAB. The comparison between experimental data and model data of each lump under the condition of temperature 500°C and residence time 10 hours, as an example, was expressed in Figure 7. And the global error was 4.34%. It was observed that the proposed kinetic model could well fits the experimental data of heavy oil upgrading through HTO. From Figure 8, it is mentioned that the model global matching is pretty marvellous, especially for the semifinished products (HO, MO and LO), whereas the mass fractions of Gases and coke have higher dispersity. It was observed that the mass fraction of gas is above 10%, suggesting the oil weight loss during upgrading process. But the high temperature gas generated from oxidation can assist displacing the oil to enhance oil recovery.

The kinetic model shows a great correlation between experimental data and Arrhenius equation suggested from Figure 8 for every proposed reaction. The results including kinetic parameters were expressed in Table 2, which is in the range of previous study mentioned in Tirado's summary[16].
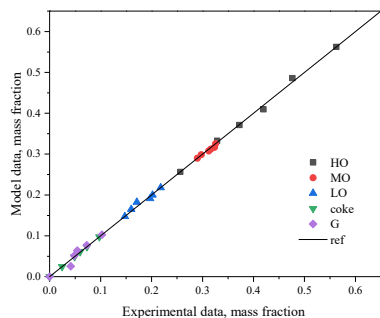
Figure 7. Comparison between experimental and model data (mass fraction) from the different lumps.
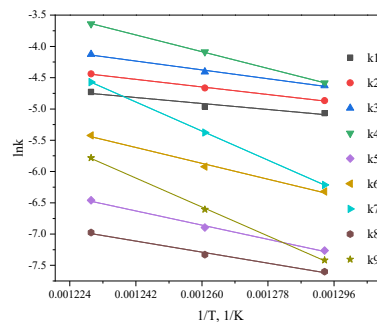
Figure 8. The kinetic model fitting of all reactions.

Table 2. The kinetic parameters of heavy oil upgrading.

Reaction constant (1/h)	Temperature (°C)			Pre-exponential factor (1/h)	Activation energy	
	500	520	540	A (1/h)	Ea (kJ/mol)	R^2
1	0.00632	0.00702	0.00887	5.91	44.13	0.947
2	0.00771	0.00943	0.01183	46.20	55.96	0.998
3	0.00983	0.01224	0.01621	249.88	65.30	0.993
4	0.01021	0.01680	0.02630	2.30E+06	123.67	0.999
5	0.00072	0.00104	0.00161	8.43E+03	104.92	0.996
6	0.00183	0.00273	0.00449	1.46E+05	117.19	0.994
7	0.00240	0.00555	0.01241	6.41E+11	214.71	0.999
8	0.00053	0.00070	0.00099	159.17	81.59	0.992
9	0.00060	0.00135	0.00308	1.66E+11	213.83	0.999

4. Conclusion

The viscosity reducing law of heavy oil upgrading and the kinetic model was studied which can provide some parameters for heavy oil production during air injection.

(1) The Xinjiang heavy oil in a porous medium was investigated for reaction conditions employing temperatures in the range from 500 to 540 °C and residence time between 4 and 16 hours. Liquid products showed an obvious increase in the fraction into LO and MO. The produced gases account for about 10% of the mass fraction.

(2) The thermal oxidation produces a significant increase in heavy oil quality especially in viscosity that is lowered between one to two orders of magnitude for the studied conditions, which can assist the development of heavy oil. The upgrading mechanism of heavy oil is mainly the destruction of aromatic ring structure.

(3) For establishing simplified reaction pathways, a five lump kinetic model was successfully used to predict the composition of products of heavy oil high temperature oxidation in a porous medium with a global error of 4.34%. Then the reaction rate constants were calculated to get the activation energy and pre-exponential factor of reactions. And the activation energies of gases generation reactions,

R_4, R_7 and R_9, were 123.67 kJ/mol, 214.71 kJ/mol and 213.83 kJ/mol, respectively.

Nomenclature list	
TG	**Thermogravimetry**
DSC	**Differential scanning calorimeter**
ARC	**Accelerating rate calorimeter**
LTO	**Low temperature oxidation**
FD	**Fuel deposition**
HTO	**High temperature oxidation**
HO	**Heavy components of oil**
MO	**Medium components of oil**
LO	**Light components of oil**

References

1. PU W, GONG X, CHEN Y, et al. Oxidation kinetic evaluation of the low temperature oxidized products of Tahe heavy oil characterized by the distributed activation energy model [J]. Journal of Petroleum Science and Engineering, 2019, 181.

2. CHEN Y, PU W, LIU X, et al. Specific kinetic triplet estimation of Tahe heavy oil oxidation reaction based on non-isothermal kinetic results [J]. Fuel, 2019, 242: 545-52.

3. PU W, GONG X, CHEN Y, et al. Non-isothermal pyrolysis and combustion kinetics of heavy oil and its low temperature oxidation products by thermal analyses [J]. Petroleum Science and Technology, 2019, 38(4): 398-404.

4. [PU W, ZHAO S, HU L, et al. Thermal effect caused by low temperature oxidation of heavy crude oil and its in-situ combustion behavior [J]. Journal of Petroleum Science and Engineering, 2020, 184.

5. WANG C, LIU H, PANG Z, et al. Enhance Oil Recovery for Steam Flooding: Low-Temperature Oxidative Decomposition of Heavy Oil with Air Injection [J]. Energy & Fuels, 2015, 29(10): 6242-9.

6. ZHAO S, PU W, VARFOLOMEEV M A, et al. Oxidation characteristics of heavy oil and its SARA fractions during combustion using TG-FTIR [J]. Journal of Petroleum Science and Engineering, 2020, 192.

7. ZHAO S, GAO H, PU W, et al. Isothermal oxidation behavior of heavy crude oil and its low-temperature oxidized oils: Implications for in-situ upgrading of heavy oil [J]. Fuel, 2022, 313.

8. PU W, YUAN C, JIN F, et al. Low-Temperature Oxidation and Characterization of Heavy Oil via Thermal Analysis [J]. Energy & Fuels, 2015, 29(2): 1151-9.

9. KöK M V, VARFOLOMEEV M A, NURGALIEV D K. Thermal characterization of crude oils by pressurized differential scanning calorimeter (PDSC) [J]. Journal of Petroleum Science and Engineering, 2019, 177: 540-3.

10. ZHAO S, PU W, PAN J, et al. Thermo-oxidative characteristics and kinetics of light, heavy, and extra-heavy crude oils using accelerating rate calorimetry [J]. Fuel, 2022, 312.

11. KöK M V, VARFOLOMEEV M A, NURGALIEV D K. Crude oil characterization using TGA-DTA, TGA-FTIR and TGA-MS techniques [J]. Journal of Petroleum Science and Engineering, 2017, 154: 537-42.

12. SADIKOV K, YUAN C, MEHRABI-KALAJAHI S S, et al. A New, Fast, and Efficient Method for Evaluating the Influence of Catalysts on In-Situ Combustion Process for Heavy Oil Recovery [Z]. SPE International Heavy Oil Conference and Exhibition. 2018: D032S43R01.10.2118/193758-MS

13. YANG M, CHAI M, YU X, et al. Insights into in-situ upgrading of bitumen in the hybrid of steam and combustion process: From experimental analysis aspects [J]. Journal of Petroleum Science and Engineering, 2022, 217.

14. HOSSEINPOUR M, HAJIALIREZAEI A H, SOLTANI M, et al. Thermodynamic analysis of in-situ hydrogen from hot compressed water for heavy oil upgrading [J]. International Journal of Hydrogen Energy, 2019, 44(51): 27671-84.

15. ZHAO S, PU W, VARFOLOMEEV M A, et al. Evaluation of heat release caused by low-temperature oxidation of heavy oil and its SARA fractions under isothermal conditions [J]. Thermochimica Acta, 2020, 690.

16. TIRADO A, YUAN C, VARFOLOMEEV M A, et al. Kinetic modeling of aquathermolysis for upgrading of heavy oils [J]. Fuel, 2022, 310: 122286.