Comparative evaluation of different non-condensable gases on thermal behaviors, kinetics, high pressure properties, and product characteristics of heavy oil

Jianbiao Chen, Xuemei Lang, Yanhong Wang, Gang Li, Zhaoling Yang, Shuanshi Fan⁎

Key Laboratory of Enhanced Heat Transfer and Energy Conservation, Ministry Education, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, Guangdong, China

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Non-condensable gas stimulation
Product analysis

A B S T R A C T

In this work, the thermal behaviors, kinetic parameters, high pressure properties, and product characteristics of Qi 40 heavy oil in air, nitrogen, carbon dioxide, oxygen-denuded air, and flue gas atmospheres were systematically and comparatively studied by thermogravimetric analysis, kinetic analysis, pressure-volume-temperature test, and stimulation experiments. The thermal decomposition of heavy oil occurred in three major zones. The comprehensive devolatilization indices of heavy oil in nitrogen, carbon dioxide, oxygen-denuded air, air, and flue gas atmospheres were 3.32 × 10⁻⁷, 2.94 × 10⁻⁷, 2.07 × 10⁻⁷, 2.30 × 10⁻⁷, and 2.58 × 10⁻⁷%K⁻³min⁻², respectively. The kinetics analysis indicated that, except for zone 2 in oxygen-denuded air, the best kinetic models of three zones were (1 − x)¹/³, (1 − x)²/⁴, and (1 − x), respectively. Pressure-volume-temperature tests displayed that the high pressure properties of heavy oil were mainly influenced by the gas solubility effects at low temperatures, and the heating effects at high temperatures. Moreover, Fourier transform infrared spectra, crude oil group, element, and gas chromatography analysis on products from stimulation experiments of heavy oil all showed that the product characteristics might be influenced by the existence of oxygen in the non-condensable gases. The results of this study provided useful information for potential application of non-condensable gases injection on thermal enhanced oil recovery.

1. Introduction

Along with the continuous development of the global economy, the rapid growth of energy demand prompted the exploitation of new possible petroleum resources. As an alternative energy resource, heavy oil has attracted a wide attention in recent years for its huge reserves all over the world [1]. Feasible exploitation techniques have been widely developed for heavy oil recovery [2]. Because of some special properties of heavy oil, including high density, high viscosity, and poor fluidity, thermal recovery seems to be one of the most potential ways [3]. Among various thermal enhanced oil recovery techniques, steam stimulation and steam flooding are the two most popular methods [4]. The practices in the steam exploitation have proven that the advantages are obvious in the early stage, but the water cut will rise rapidly after multi-run injection. Recently, concerns over the adverse influences in the steam mining later period have led investigators to make great efforts in heavy oil production by thermal recovery assisting with non-condensable gas injection [5]. Compared to heavy oil recovery by steam injection, gas injection can effectively reduce heat loss and get a larger sweep volume [6].

Heavy oil recovery by non-condensable gas injection is an effective technique to enhance oil recovery (EOR) [7]. It eventually utilized the energy carried by the non-condensable gas with a high temperature to heat heavy oil reservoir, reduce oil viscosity, and improve oil fluidity in the porous rocks [8]. As several typical gases, nitrogen (N₂), carbon dioxide (CO₂), flue gas, and air were considered in heavy oil production for extensive sources, low cost, and good oil recovery [9]. In the literature [10], the dissolving capacity and viscosity reducing effect of CO₂ on heavy oil have been compared with those of N₂, and found that CO₂ was much more effectively. CO₂ can recover more oil via the generation of miscibility by lowering the interfacial tension (IFT) [11]. Generally, to realize the target of EOR, the gas should be preheated to the certain temperature on the ground. From the viewpoint of energy conservation, the flue gas with high temperature has been popularly used as a thermal fluid to increase heavy oil recovery [12]. Further, to avoid the heat loss in the gas transmission, injecting air to the oil reservoir was brought into operation, and EOR was achieved mainly due to the steam flooding and viscosity reduction as a result of heat
produced by the in-situ combustion (ISC) of crude oil [13]. As pointed out by Fan et al. [14], almost all the oxygen (O2) in the injection gas was consumed by the low-temperature oxidation of heavy oil, which could effectively avoid the O2 breakthrough and consequently safety issues during the air injection process. But in fact, the combustion process of heavy oil in the reservoir is difficult to be monitored, so that the O2 breakthrough does exist. In this case, the O2 addition reactions between crude oil and O2 remaining in gas would result in a dramatic increase of the oil viscosity with the formation of heavier oil fractions [15]. Additionally, the air injected with a high O2 would make the combustion process uncontrollable, and a large number of petroleum resources were also wasted. To gain a good heavy oil recovery, using heavy oil as feedstock. Kok and Gundogar [16] have studied the thermal behaviors, kinetic parameters, high temperature oxidation, and the pyrolysis process occurred in two zones of the distillation and cracking. Kok [17] studied thermal kinetics of heavy oil by thermogravimetric analyzer (TGA) at distinct heating rates. It was found that activation energies generated for the high temperature oxidation region were in the range of 48.5–151.0 kJ mol\(^{-1}\) at three different heating rates. In the study of Fan et al. [18], the thermal oxidative decomposition kinetics of heavy oil were analyzed by the distributed activation energy model (DAEM). It was observed that the apparent activation energies at low temperatures were around 100 kJ mol\(^{-1}\), and at high temperatures were about 190–230 kJ mol\(^{-1}\). With regard to the phase properties, Riyahin et al. [19] presented a new set of correlation for estimating crude oils properties based on some experimental pressure-volume-temperature (PVT) data. It was found out that the new correlations were more accurate than the other ones. Cao and Gu [20] evaluated the effects of temperature on the phase property, mutual interactions, and oil recovery of a light crude oil-CO\(_2\) system. It was found that the saturation pressure and oil-swelling factor increased almost linearly with CO\(_2\) concentration. As for products characterization, Pu et al. [21] have detected the content of O\(_2\), CO\(_2\), CO, and hydrocarbon gas (C\(_1\)–C\(_4\)) of the produced gases from the low temperature oxidation of heavy oil. Khansari et al. [22] performed product estimation for the low temperature oxidation of Lloydminster heavy oil. The elemental analysis on reaction residues suggested that aldehyde, alcohols and ketones, hydroperoxide and carboxylic acids, ketones and hydro-peroxide are the major products of the first, second, third, and fourth subzone, respectively. Yang et al. [23] have made a comprehensive analysis of the properties of crude oil in oxidation experiments, and found that the intermediate components (C\(_7\)–C\(_{17}\)) made a great contribution to crude oil cracking. Although the thermal behaviors, kinetics, phase properties, and product characteristics of heavy oils have been reported, previous studies were just carried out under N\(_2\), CO\(_2\), or air condition.

To date, a number of studies have been performed on the thermal behaviors, kinetics, phase properties, and products characterization using heavy oil as feedstock. Kok and Gundogar [16] have studied the thermal behaviors of Turkish crude oils in air and N\(_2\) atmospheres via differential scanning calorimetry (DSC). From DSC curves, the combustion process of Turkish oils could be divided into two zones of the low temperature oxidation and high temperature oxidation, and the pyrolysis process occurred in two zones of the distillation and cracking. Kok [17] studied thermal kinetics of heavy oil by thermogravimetric analyzer (TGA) at distinct heating rates. It was found that activation energies generated for the high temperature oxidation region were in the range of 48.5–151.0 kJ mol\(^{-1}\) at three different heating rates. In the study of Fan et al. [18], the thermal oxidative decomposition kinetics of heavy oil were analyzed by the distributed activation energy model (DAEM). It was observed that the apparent activation energies at low temperatures were around 100 kJ mol\(^{-1}\), and at high temperatures were about 190–230 kJ mol\(^{-1}\). With regard to the phase properties, Riyahin et al. [19] presented a new set of correlation for estimating crude oils properties based on some experimental pressure-volume-temperature (PVT) data. It was found out that the new correlations were more accurate than the other ones. Cao and Gu [20] evaluated the effects of temperature on the phase property, mutual interactions, and oil recovery of a light crude oil-CO\(_2\) system. It was found that the saturation pressure and oil-swelling factor increased almost linearly with CO\(_2\) concentration. As for products characterization, Pu et al. [21] have detected the content of O\(_2\), CO\(_2\), CO, and hydrocarbon gas (C\(_1\)–C\(_4\)) of the produced gases from the low temperature oxidation of heavy oil. Khansari et al. [22] performed product estimation for the low temperature oxidation of Lloydminster heavy oil. The elemental analysis on reaction residues suggested that aldehyde, alcohols and ketones, hydroperoxide and carboxylic acids, ketones and hydro-peroxide are the major products of the first, second, third, and fourth subzone, respectively. Yang et al. [23] have made a comprehensive analysis of the properties of crude oil in oxidation experiments, and found that the intermediate components (C\(_7\)–C\(_{17}\)) made a great contribution to crude oil cracking. Although the thermal behaviors, kinetics, phase properties, and product characteristics of heavy oils have been reported, previous studies were just carried out under N\(_2\), CO\(_2\), or air condition.

In view of these, the thermal behaviors, kinetic parameters, high pressure properties, and product characteristics of heavy oil in air, N\(_2\), CO\(_2\), oxygen-denuded air, and flue gas were systematically and comparatively evaluated. The knowledge obtained from this work could present some basic information for potential application of non-condensable gases on thermal enhanced oil recovery.

2. Materials and methods

This section gave a detailed introduction for the heavy oil sample, non-condensable gases, thermal analysis method, kinetic theory, pressure-volume-temperature (PVT) test device and method, and non-condensable gas stimulation experiments.

2.1. Raw materials

The heavy oil sample studied in this work was selected from Qi 40
block of Liaohai oil field in the northeast China. The relations of viscosity vs. temperature for Qi 40 heavy oil were studied, and the data were shown in Table 1.

The non-condensable gases used in this work were air, \( N_2 \), \( CO_2 \), \( O_2 \)-denuded air, and flue gas. These gases were provided by Guangzhou Zhourong Gas Co., Ltd. (Guangdong Province, China). The composition of various non-condensable gases were given in Table S-1. It can be observed that the \( O_2 \)-denuded air consisted of 9.99 vol\% \( O_2 \) and 90.01 vol\% \( N_2 \). The flue gas was simulated by 3.00 vol\% \( O_2 \), 11.93 vol\% \( CO_2 \), and 85.07 vol\% \( N_2 \).

2.2. Experimental apparatus and procedures

According to literatures, the thermal behaviors, kinetic parameters, high pressure properties, and product characteristics of fuels in varied atmospheres could be effectively evaluated by TGA, CR method, PVT test, and stimulation experiments, respectively.

2.2.1. Thermal analysis and kinetic theory

Thermal analysis experiments of Qi 40 heavy oil were carried out on the NETZSCH STA 449C simultaneous thermogravimetric analyzer (TGA). In order to reduce the influences caused by the heat and mass transfer, the initial weight of heavy oil was maintained at a small value of 6 ± 0.2 mg. The heavy oil placed in the crucible of TGA was heated up from 300 K to 873 K at the heating rate of 10 K min\(^{-1}\). The carrier gases were air, \( N_2 \), \( CO_2 \), \( O_2 \)-denuded air, and flue gas respectively, with a flow rate of 50 mL min\(^{-1}\). For each thermal analysis, the blank experiment without sample in the crucible was performed to gain TG baseline. All the thermal degradation tests were repeated at least twice to guarantee the reproducibility of the thermal data.

The kinetics analysis of the thermal decomposition of heavy oil can acquire more information from the thermal analysis experiments. Using thermal data, the thermal decomposition process of Qi 40 heavy oil in different gases can be simulated by the conversion rate equation [24].

\[
\frac{dx}{dt} = k(T) f(x) = \frac{dx}{dt} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(x) \tag{1}
\]

where \( x \) is the conversion degree of individual thermal degradation zone, \( dx/dt \) is the conversion rate, which can be calculated as a function of the rate constant \( k(T) = A \exp(-E/RT) \) and differential kinetic model \( f(x) \) [25]. \( A \), \( E \), and \( R \) are the pre-exponential factor, activation energy, universal gas constant, and absolute temperature, respectively [26]. As for the non-isothermal experiments performed at \( \beta = \frac{dT}{dt} \), the conversion rate equation can be rearranged to the right part of Eq. (1).

Coats-Redfern (CR) method was adopted to calculate the kinetic parameters of the thermal degradation process of heavy oil in different gases. The equation is [27]:

\[
\ln \left( \frac{g(x)}{T^2} \right) = \ln \left[ \frac{AR}{E} \left(1 - \frac{2RT}{E}\right) \right] - \frac{E}{RT} \tag{2}
\]

Here, \( g(x) \) is the integral form of the kinetic function \( f(x) \). \( 2RT/E \) at current temperature range of the thermal degradation of heavy oil was small, thus \( 1 - 2RT/E \approx 1 \) and Eq. (2) can be simplified:

\[
\ln \left( \frac{g(x)}{T^2} \right) = \ln \left[ \frac{AR}{E} \right] + \frac{E}{RT} \tag{3}
\]

Prior to the kinetics analysis, the conversion degrees \( x \) of individual thermal decomposition zone were recalculated as a function of the temperature [28]. The range of \( x \) applied in the thermal decomposition kinetics analysis was in 5–95% [29]. In Eq. (3), once the best model function in Table S-2 [30] for individual zone was selected, \( E \) and \( A \) can be gained from the slope \( -E/\beta \) and intercept \( \ln[AR/\beta E] \) with the highest correlation coefficient \( R^2 \), respectively.

2.2.2. Pressure-volume-temperature tests

Pressure-volume-temperature (PVT) test is an important means to investigate the influence of non-condensable gas on the high pressure characteristics of heavy oil [31]. The solubility of gas in heavy oil (S), volume ratio (VR), and viscosity after gas saturation can be gained by PVT analysis apparatus. As shown in Fig. 1, the PVT apparatus is composed primarily of gas supply, buffering, PVT test, and data acquisition. The PVT test unit was the core part of overall system, and made up of a visual reactor and several temperature controlling devices.

Based on SY/T 5542-2009, about 175 mL dehydrated heavy oil was placed into the visual reactor. After evacuation, air, \( N_2 \), \( CO_2 \), \( O_2 \)-denuded air, and flue gas were respectively injected to the reactor till the required pressure of 3.0 MPa. The gas temperature (\( T_1 \)) and pressure (\( P_1 \)) in the reactor were detected by the temperature and pressure sensors, respectively. Then, the reactor was heated up to the desired temperatures (313, 373, 423, and 473 K) and maintained at least 6 h. The heavy oil in the reactor would fully dissolve gas until saturating, then record gas temperature (\( T_2 \)) and pressure (\( P_2 \)) at the moment. Using related temperature and pressure data, and the equation of state, the values of \( S \) and VR can be calculated.

\[
PV = n_0RT \tag{4}
\]

where \( P \), \( V \), \( Z \), \( n \), and \( T \) are the pressure, volume, compressibility factor, mole, and temperature of gas, respectively.

The molar variation of gas before and after PVT test (\( \Delta n \)) is

\[
\Delta n = n_1 - n_2 = \frac{1}{R} \left( \frac{P_1V_{11} - P_2V_{22}}{Z_1 - Z_2} \right) \tag{5}
\]

where \( n_1, V_{11}, Z_1, \) and \( T_1 \) represent the mole, volume, compressibility factor, and temperature of gas before PVT test, respectively. \( n_2, V_{22}, Z_2, \) and \( T_2 \) are the similar parameters after PVT test.

The value of \( S \) (m\(^3\) m\(^{-3}\)) can be gained as follows:

\[
S = \frac{\Delta V}{V_1} = \frac{22.4 \times \Delta n \times 10^3}{V_1} \tag{6}
\]

where \( \Delta V \) and \( V_1 \) are the volumes of dissolved gas and heavy oil, respectively.

The calculation formula of VR (m\(^3\) m\(^{-3}\)) is

\[
VR = \frac{V_2}{V_1} \tag{7}
\]

In Eq. (7), \( V_2 \) is the volume of heavy oil after gas saturation.

2.2.3. Non-condensable gas stimulation experiments

To gain an insight into the influence of non-condensable gas on chemical components of heavy oil, the stimulation experiments in air, \( N_2 \), \( CO_2 \), \( O_2 \)-denuded air, and flue gas were carried out at different temperatures of 373, 423, and 473 K. As shown in Fig. 2, the schematic diagram of the non-condensable gas stimulation on Qi 40 heavy oil consisted of four parts, such as carrier gas, high-pressure reactor, temperature controller, and temperature and pressure data acquisition. Prior to the non-condensable gas stimulation experiments, the experimental devices were connected, and then the tightness was carefully checked. About 50 mL heavy oil was placed into the high-pressure reactor, and then the air in the reactor was pumped clearly. After that, air, \( N_2 \), \( CO_2 \), \( O_2 \)-denuded air, and flue gas were respectively injected into the reactor till the desired pressure. This accomplished, the reactor was

<table>
<thead>
<tr>
<th>Temperature/K</th>
<th>303</th>
<th>313</th>
<th>323</th>
<th>333</th>
<th>343</th>
<th>353</th>
<th>363</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity/mPas</td>
<td>13.680</td>
<td>4500</td>
<td>1536</td>
<td>660</td>
<td>280</td>
<td>241</td>
<td>143</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>373</td>
<td>383</td>
<td>403</td>
<td>423</td>
<td>443</td>
<td>473</td>
<td></td>
</tr>
<tr>
<td>Viscosity/mPas</td>
<td>101.6</td>
<td>84.7</td>
<td>49.6</td>
<td>31.2</td>
<td>19.7</td>
<td>9.8</td>
<td></td>
</tr>
</tbody>
</table>
heated up to 373, 423, and 473 K, respectively, and remained at the temperature for a long time. During the experiments, the temperature and pressure were real-time monitored by the temperature and pressure sensors, respectively. The reaction temperature can be timely corrected by the temperature controller to insure a successful reaction.

After above procedures, the liquid and gas products were collected for subsequent analysis. The surface chemical structure, crude oil group (i.e. SARA fractions, Saturates, Aromatics, Resins, and Asphaltenes), and elemental compositions (Carbon, Hydrogen, Oxygen, Nitrogen, and Sulfur) of liquid products were analyzed using Nicolet 6700 Flex FTIR (Thermo Fisher Scientific, USA), Self-build SARA evaluation device, and Vario Macro cube CHNS elemental analyzer (Elementar, Germany), respectively. The compositions of gas products were off-line analyzed through the GC 9800 gas chromatography (Shanghai Kechuang Chromatograph Instrument Co., Ltd, Shanghai, China) with a thermal conductivity detector (TCD).

3. Results and discussion

The paper discussed the effects of different non-condensable gases on the thermal behaviors and kinetics, PVT characteristics, and products properties of Qi 40 heavy oil.

3.1. Thermal decomposition of heavy oil in different non-condensable gases

The thermal decomposition process of Qi 40 heavy oil at 10 K min$^{-1}$ in air, N$_2$, CO$_2$, O$_2$-denuded air, and flue gas were described with TG (Thermogravimetric) and DTG (Differential thermogravimetric) curves. To quantitatively analyze the thermal performance of heavy oil, some characteristic parameters were calculated from the TG-DTG curves.

3.1.1. Thermal decomposition behaviors

Fig. 3 indicated that, the thermal degradation process of Qi 40 heavy oil in different non-condensable gases could be divided into three zones of dehydration (< 400 K), distillation (in the temperature range of 400–660 K), and cracking (> 660 K). The similar findings have also been reported in the thermal decomposition of light crude oils [32]. It was evident that there existed an overlap between distinct zones of the decomposition of Qi 40 heavy oil. The main reason was that the chemical components in heavy oil were complex, so that some function groups decomposed at near temperature range. Overall, the thermal curves in different atmospheres exhibited a similar trend during the temperature interval of heating.

Fig. 1. Flow chart of the PVT experiment: (1) Cylinder; (2) Valve; (3) Buffering container; (4) High pressure reactor; (5) Pressure sensor; (6) Thermocouple; (7) Temperature controller; (8) Gas chromatography (GC); (9) Data acquisition unit; (10) Computer.

Fig. 2. Schematic diagram of the non-condensable gas stimulation on Qi 40 heavy oil: (1) Cylinder; (2) Pressure reducing valve; (3) Valve; (4) High pressure reactor; (5) Temperature controller; (6) Pressure sensor; (7) Thermocouple; (8) Computer.

For better describing the thermal behaviors of Qi 40 heavy oil under the influence of varied non-condensable gases, some characteristic parameters obtained from the TG-DTG curves [33] were listed in Table 2. The moisture content of the sample was low, which had a negligible effect on the overall thermal decomposition performance, so the thermal behaviors analysis for moisture release was ignored [34]. It was seen from Table 2 that distinct gases had a slight effect on $T_{i2}$, $T_{f2}$, $T_{i3}$, and $T_{f3}$, while greatly affected $T_{p2}$ and $T_{p3}$. The $W_r$ values for heavy oil decomposed in air, N$_2$, CO$_2$, O$_2$-denuded air, and flue gas were 12.75%, 9.43%, 9.26%, 20.38%, and 14.07%, respectively. It was obvious that more solid residues after thermal decomposition experiments would be generated as a result of O$_2$ in the carrier gas. With O$_2$ concentration increasing, the value of $W_r$ increased first and then decreased. The main reason for this result could be attributed to the absorption and oxidation between O$_2$ and heavy oil, which could also be verified by the maximum weight loss rate at zone 3 ($-R_{p3}$). Unlike $W_r$, the value of $-R_{p3}$ generally decreased with an increase of O$_2$ concentration, and then resulting in more residues.
Moreover, the comprehensive devolatilization index \( D \) was used to evaluate the thermal degradation performance of heavy oil in diverse carrier gases. The calculation formula is [35]

\[
D = \frac{(-R_p) \times (-R_v)}{T_i \times T_p \times \Delta T}
\]  

(8)

where \( -R_p, -R_v, T_i, T_p, \) and \( \Delta T \) have been defined in Table 2.

For multiple zones of the thermal degradation, Eq. (8) can be further rearranged [36]

\[
D = \sum WL_i \times D_i
\]  

(9)

In Eq. (9), \( WL_i \) is weight loss percentage of each zone in the total weight loss; \( D_i \) is the index \( D \) of each zone. The higher index \( D \) is, the better devolatilization performance is.

As seen from Table 3, the devolatilization performance orders of Qi 40 heavy oil decomposed in non-condensable gases were ranked by \( \text{O}_2\)-denuded air > flue gas > air > \( \text{CO}_2 > \text{N}_2 \) at zone 2, while \( \text{O}_2\)-denuded air < air < flue gas < \( \text{CO}_2 < \text{N}_2 \) at zone 3. No matter which gas used, the \( D \) value of zone 3 was higher than that of zone 2, indicating that the overall devolatilization performance of heavy oil was dominated by zone 3. The \( D \) values of the overall thermal degradation process of heavy oil in air, \( \text{N}_2, \text{CO}_2, \text{O}_2\)-denuded air, and flue gas were \( 2.30 \times 10^{-7}, \ 3.32 \times 10^{-7}, \ 2.94 \times 10^{-7}, \ 2.07 \times 10^{-7} \), and
The kinetic parameters calculated were accurate [38].

As seen from Table 4, the E values of zone 1 of the thermal decomposition of heavy oil were close in air, N\textsubscript{2}, CO\textsubscript{2}, O\textsubscript{2}-denuded air, and flue gas, indicating that the influences of atmospheres on the E values of zone 1 were negligible. In the research of Chen et al. [39], the E value of the first thermal decomposition zone of petrochemical wastewater sludge in CO\textsubscript{2} was 60.73 kJ mol\textsuperscript{-1}. However, the E values of zone 2 were quite different in air, N\textsubscript{2}, CO\textsubscript{2}, O\textsubscript{2}-denuded air, and flue gas. Similarly, the E values of zone 3 decomposed in varied atmospheres were also diverse. With the thermal decomposition proceeding, the E values decreased first and then increased as a whole in either atmosphere. The similar findings were reported in the thermal degradation of petrochemical wastewater sludge in either CO\textsubscript{2} [39] or N\textsubscript{2} [40]. Similarly, as reported by Fan et al. [18], the E values was lower at low temperatures, while increased significantly at high temperatures. For checking the accuracy of the kinetics analysis, the comparison between experimental data and theoretical values were performed. According to Eq. (1), the x

<table>
<thead>
<tr>
<th>Atmospheres</th>
<th>Zone 2</th>
<th>Zone 3</th>
<th>W\textsubscript{2} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>410.3</td>
<td>2.46</td>
<td>653.3</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>416.1</td>
<td>2.28</td>
<td>666.1</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>396.1</td>
<td>2.31</td>
<td>668.1</td>
</tr>
<tr>
<td>O\textsubscript{2}-denuded air</td>
<td>394.1</td>
<td>2.37</td>
<td>674.1</td>
</tr>
<tr>
<td>Flue gas</td>
<td>414.9</td>
<td>2.19</td>
<td>659.4</td>
</tr>
</tbody>
</table>

\[ T_a, \text{ the initial decomposition temperature.} \]
\[ T_p, \text{ the peak temperature of each zone;} \]
\[ \Delta T, \text{ the temperature range at half value of each zone;} \]
\[ W, \text{ the residual weight after experiment.} \]

2.58 \times 10^{-7}\% K^{-3} min^{-2}, respectively. The results indicated that the devolatilization performance of Qi 40 heavy oil might be influenced by the existence of O\textsubscript{2} in the carrier gas.

3.1.2. Thermal decomposition kinetics

For the sake of ensuring a successful implement, calculating the kinetic parameters from the thermal decomposition of Qi 40 heavy oil is highly required for numerical simulation to design and optimize the operating conditions [37]. The kinetic parameters, including E, A, and f (x), that obtained with the highest R\textsuperscript{2} were shown in Table 4. Data of R\textsuperscript{2} shown in Table 4 were in the range of 0.9868–0.9979, indicating that the kinetic parameters calculated were accurate [38].

<table>
<thead>
<tr>
<th>Atmospheres</th>
<th>Temperature range ΔT/K</th>
<th>Activation energy E/kJ mol\textsuperscript{-1}</th>
<th>Pre-exponential factor A/s\textsuperscript{-1}</th>
<th>Kinetic model f(x)</th>
<th>Correlation coefficient R\textsuperscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>300.1–409.8</td>
<td>52.04</td>
<td>2.13 \times 10\textsuperscript{5}</td>
<td>(1 – x)\textsuperscript{1/3}</td>
<td>0.9975</td>
</tr>
<tr>
<td></td>
<td>410.3–653.3</td>
<td>37.62</td>
<td>0.89</td>
<td>(1 – x)\textsuperscript{2/3}</td>
<td>0.9983</td>
</tr>
<tr>
<td></td>
<td>653.8–795.8</td>
<td>131.98</td>
<td>1.09 \times 10\textsuperscript{7}</td>
<td>(1 – x)</td>
<td>0.9934</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>300.1–415.6</td>
<td>47.52</td>
<td>7.64 \times 10\textsuperscript{4}</td>
<td>(1 – x)\textsuperscript{1/3}</td>
<td>0.9720</td>
</tr>
<tr>
<td></td>
<td>416.1–666.6</td>
<td>30.26</td>
<td>0.16</td>
<td>(1 – x)\textsuperscript{2/3}</td>
<td>0.9919</td>
</tr>
<tr>
<td></td>
<td>667.1–844.6</td>
<td>162.98</td>
<td>1.79 \times 10\textsuperscript{9}</td>
<td>(1 – x)</td>
<td>0.9974</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>300.1–395.6</td>
<td>51.96</td>
<td>1.04 \times 10\textsuperscript{5}</td>
<td>(1 – x)\textsuperscript{1/3}</td>
<td>0.9868</td>
</tr>
<tr>
<td></td>
<td>396.1–667.6</td>
<td>27.97</td>
<td>3.97 \times 10\textsuperscript{10}</td>
<td>(1 – x)\textsuperscript{2/3}</td>
<td>0.9928</td>
</tr>
<tr>
<td></td>
<td>668.1–845.1</td>
<td>163.51</td>
<td>1.79 \times 10\textsuperscript{9}</td>
<td>(1 – x)</td>
<td>0.9977</td>
</tr>
<tr>
<td>O\textsubscript{2}-denuded air</td>
<td>300.1–393.6</td>
<td>44.11</td>
<td>5.49 \times 10\textsuperscript{9}</td>
<td>(1 – x)\textsuperscript{1/3}</td>
<td>0.9968</td>
</tr>
<tr>
<td></td>
<td>394.1–673.6</td>
<td>45.36</td>
<td>3.58 \times 10\textsuperscript{10}</td>
<td>(1 – x)\textsuperscript{1/3}</td>
<td>0.9939</td>
</tr>
<tr>
<td></td>
<td>674.1–800.6</td>
<td>182.16</td>
<td>5.31 \times 10\textsuperscript{10}</td>
<td>(1 – x)</td>
<td>0.9933</td>
</tr>
<tr>
<td>Flue gas</td>
<td>300.1–414.4</td>
<td>40.50</td>
<td>1.14 \times 10\textsuperscript{3}</td>
<td>(1 – x)\textsuperscript{1/3}</td>
<td>0.9928</td>
</tr>
<tr>
<td></td>
<td>414.9–651.4</td>
<td>37.64</td>
<td>4.01</td>
<td>(1 – x)\textsuperscript{2/3}</td>
<td>0.9976</td>
</tr>
<tr>
<td></td>
<td>651.9–845.4</td>
<td>127.08</td>
<td>4.27 \times 10\textsuperscript{7}</td>
<td>(1 – x)</td>
<td>0.9965</td>
</tr>
</tbody>
</table>
values could be calculated as a function of the temperature by taking advantage of the kinetic parameters in Table 4. As shown in Fig. 4, the theoretical line and experimental data were almost overlapped with each other, indicating that the kinetic parameters obtained could correctly forecast the thermal decomposition process of Qi 40 heavy oil in varied atmospheres.

3.2. Influence of non-condensable gas on PVT characteristics

The PVT characteristics of Qi 40 heavy oil in different non-condensable gases were available in Table 5. It could be observed that the S values of CO₂ in Qi 40 heavy oil at various temperatures were higher than those of air, N₂, O₂-denuded air, and flue gas. It was because that

![Fig. 4. Experimental x (scatter) and calculated x (line) from thermal degradation of Qi 40 heavy oil at 10 K min⁻¹ in (a) air, (b) N₂, (c) CO₂, (d) O₂-denuded air, and (e) flue gas.](image-url)
3.3.2. SARA fractions analysis

According to NB/SH/T 0509-2010, SARA fractions [43] were separated from Qi 40 heavy oil, and quantitatively determined. As shown in Fig. 6, the contents of saturates, aromatics, resins, and asphaltenes in raw heavy oil were 39.36, 29.61, 29.61, and 4.12 wt%, respectively. As for the stimulation tests in air, O2-denuded air and flue gas, with temperature increasing, the contents of resins and asphaltenes increased, whereas the contents of saturates and aromatics reduced. The reduction in saturates content might be related to the thermal (oxidative) decomposition, which would also generate a small amount of carbon-containing gas. With respect to the asphaltenes, the content increase could be attributed to the thermal (oxidative) degradation of aromatics and resins. Relatively, the variation of resins content was more complex, which was ascribed to the thermal (oxidative) degradation of asphaltenes and thermal (oxidative) polymerization of aromatics. Fig. 6(c) presented the effects of temperatures on the SARA contents in CO2 atmosphere. As compared with raw sample, the contents of saturates and aromatics were almost the same, while the resins content reduced, and resulted in an increase for asphaltenes.

3.3.3. Elemental analysis

Fig. 7 showed the elemental analyses of carbon (C), hydrogen (H), oxygen (O), nitrogen (N), and sulfur (S) for Qi 40 heavy oil and its liquid products from stimulation experiments in air, N2, CO2, O2-denuded air, and flue gas. It can be observed that Qi 40 heavy oil and its liquid products were mainly composed of C and H. As shown in Fig. 7(a) and (b), with the temperature increasing, the C content increased first and then decreased, but the H content gradually decreased. Fig. 7(c) displayed that, with the temperature rising, the C content increased first and then decreased, but the H content reduced first and then increased. The main reason for these changes could be mainly ascribed to the cross-linking reactions between the hydroxyl groups (−OHs) at low temperatures, and the thermal degradation of carbon-containing groups at high temperatures. In O2-denuded air and flue gas atmospheres, the contents of H both decreased with the temperature increasing which was ascribed to the thermal oxidative degradation of C−H and the cross-linking reactions between −OHs. However, no rule could be observed about the C contents in the samples as shown in Fig. 7(c) and (d).

3.3.4. Gas compositions analysis

The gas from air, N2, CO2, O2-denuded air, and flue gas stimulation experiments on Qi 40 heavy oil at different temperatures were off-line.

Table 5

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Solubility S (m3 m−3)</th>
<th>Volume ratio VR (m3 m−3)</th>
<th>Viscosity (mPas)</th>
<th>Viscosity-reducing ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air-313K</td>
<td>1.12</td>
<td>1.10</td>
<td>4532</td>
<td>−0.71</td>
</tr>
<tr>
<td>Air-373K</td>
<td>1.67</td>
<td>1.15</td>
<td>105.3</td>
<td>−3.64</td>
</tr>
<tr>
<td>Air-423K</td>
<td>2.03</td>
<td>1.17</td>
<td>52.3</td>
<td>−35.58</td>
</tr>
<tr>
<td>Air-473K</td>
<td>1.89</td>
<td>1.21</td>
<td>13.7</td>
<td>−39.80</td>
</tr>
<tr>
<td>N2-313K</td>
<td>1.04</td>
<td>1.09</td>
<td>4407</td>
<td>2.07</td>
</tr>
<tr>
<td>N2-373K</td>
<td>0.86</td>
<td>1.08</td>
<td>95.6</td>
<td>5.91</td>
</tr>
<tr>
<td>N2-423K</td>
<td>0.77</td>
<td>1.11</td>
<td>29.2</td>
<td>6.41</td>
</tr>
<tr>
<td>N2-473K</td>
<td>0.37</td>
<td>1.10</td>
<td>9.2</td>
<td>12.12</td>
</tr>
<tr>
<td>CO2-313K</td>
<td>10.73</td>
<td>1.19</td>
<td>4379</td>
<td>2.67</td>
</tr>
<tr>
<td>CO2-373K</td>
<td>8.52</td>
<td>1.21</td>
<td>89.1</td>
<td>12.30</td>
</tr>
<tr>
<td>CO2-423K</td>
<td>6.44</td>
<td>1.20</td>
<td>29.7</td>
<td>4.81</td>
</tr>
<tr>
<td>CO2-473K</td>
<td>2.23</td>
<td>1.21</td>
<td>8.8</td>
<td>10.20</td>
</tr>
<tr>
<td>O2-denuded air-313K</td>
<td>0.93</td>
<td>1.04</td>
<td>4425</td>
<td>1.67</td>
</tr>
<tr>
<td>O2-denuded air-373K</td>
<td>1.30</td>
<td>1.12</td>
<td>92.1</td>
<td>9.35</td>
</tr>
<tr>
<td>O2-denuded air-423K</td>
<td>1.43</td>
<td>1.13</td>
<td>29.8</td>
<td>4.49</td>
</tr>
<tr>
<td>O2-denuded air-473K</td>
<td>0.20</td>
<td>1.17</td>
<td>9.6</td>
<td>2.04</td>
</tr>
<tr>
<td>Flue gas-313K</td>
<td>2.26</td>
<td>1.10</td>
<td>4398</td>
<td>2.27</td>
</tr>
<tr>
<td>Flue gas-373K</td>
<td>3.72</td>
<td>1.13</td>
<td>91.6</td>
<td>9.84</td>
</tr>
<tr>
<td>Flue gas-423K</td>
<td>1.31</td>
<td>1.14</td>
<td>30.9</td>
<td>0.96</td>
</tr>
<tr>
<td>Flue gas-473K</td>
<td>1.06</td>
<td>1.17</td>
<td>9.3</td>
<td>5.10</td>
</tr>
</tbody>
</table>
detected by GC apparatus, and demonstrated in Table 6. The results showed that CH4 and H2 were not produced during the gas stimulation. As illustrated in Table 6, in air, O2-denuded air, and flue gas atmospheres, the production of CO2 increased with increasing the experimental temperatures, but the concentration of O2 accordingly decreased. The results indicated that the production of CO2 could be ascribed to the oxidation of carbon fractions from heavy oil. There was still one thing should be concerned. In the air and O2-denuded air atmospheres, the depletion of O2 was larger than the yield of CO2, while the opposite was found in the flue gas atmosphere. In general, the solubility of N2 in heavy oil was much lower than that of CO2, so the concentration of N2 in the gas phase could be thought to remain

Fig. 5. FTIR spectra for Qi 40 heavy oil and its liquid products from (a) air, (b) N2, (c) CO2, (d) O2-denuded air, and (e) flue gas stimulation at different temperatures.
During air and O₂-denuded air stimulation experiments, part CO₂ generated by the oxidation was dissolved into the heavy oil, so the concentration of N₂ in the gas products would be higher than that in the experimental gas. As for the flue gas stimulation, certain CO₂ would be dissolved into the heavy oil at the beginning of the experiments. With the temperatures increasing, pre-dissolved CO₂ would release from the oil phase. It was the reason which made the CO₂ yield in the gas products higher, and the concentration of N₂ lower. With regard to the experiment in N₂, the CO₂ production similarly increased with the experimental temperatures increasing.

In CO₂ atmosphere, there were a small amount of N₂ and O₂ existing in the gas products at 373 K and 473 K. The possible reasons might be
due to the leakage of air during the process of sampling or injecting gas samples into GC device. Here, it could not be confirmed that whether the chemical reactions existed or not during the CO$_2$ stimulation. Considering that the reaction temperatures were low, the thermal decomposition of C=O was very faint, and the production of carbon-containing gas was very low. Thus, as demonstrated from the FTIR spectra in Fig. 5(c), the absorption peaks of C=O remained identical for Qi 40 heavy oil and its liquid products at different temperatures. Through comparing the CO$_2$ concentrations in the gas products with the experimental gas compositions in Table S-1, it was found that certain CO$_2$ would be generated from the stimulation experiments in O$_2$-denuded air and flue gas.
4. Conclusions

Through performing thermogravimetric analysis, kinetics analysis, PVT test, and stimulation experiments on heavy oil from Qi 40 block of Liaohe oil field in air, N_{2}, CO_{2}, O_{2}-denuded air, and flue gas atmospheres, the following conclusions were summarized:

(1) The thermal events of heavy oil in different atmospheres could be divided into three zones of dehydration, distillation, and cracking. The devolatilization performance orders were ranked by O_{2}-denuded air > flue gas > air > CO_{2} > N_{2} at zone 2, while O_{2}-denuded air < air < flue gas < CO_{2} < N_{2} at zone 3. The kinetics analysis showed that, except for zone 2 in O_{2}-denuded air, the most fitting kinetic models of dehydration, distillation, and cracking of heavy oil were (1−x)^{1/3}, (1−x)^{3/4}, and (1−x), respectively.

(2) PVT tests showed that the high pressure properties of heavy oil were mainly controlled by the gas solubility effects at low temperatures, and the heating effects at high temperatures. Since the oxygen addition reactions between heavy oil and air existed, the viscosity of heavy oil after PVT tests increased.

(3) Through FTIR analysis, the chemical groups in liquid products from air, O_{2}-denuded air, and flue gas stimulation experiments have all displayed to increase first and then decrease, but which remained relatively identical from N_{2} and CO_{2} stimulation experiments. As for SARA fractions, the variation trends of contents with temperature in CO_{2} were quite distinct from those in air, N_{2}, O_{2}-denuded air, and flue gas. Elemental analysis indicated that heavy oil and its liquid products were mainly composed of C and H. Gas compositions analysis showed that CO_{2} was generated during non-condensable gas stimulation experiments. There CO_{2} would be dissolved into the heavy oil at low temperatures, and then some dissolved CO_{2} would release from the oil phase with the temperatures increasing.

This work investigated the thermal behaviors, kinetic parameters, high pressure properties, and product characteristics of heavy oil in several common non-condensable gases, which could provide useful information for the background of gas injection on thermal enhanced oil recovery.


[38] Vyazovkin S, Burnham AK, Criado JM, et al. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. Thermochim Acta 2011;520:1–19.


