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Mechanism investigation of steam flooding heavy oil by comprehensive molecular characterization

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ABSTRACT

Steam flooding is a widely used technique to enhance oil recovery of heavy oil. Thermal viscosity reduction and distillation effect are considered as two main displacement mechanisms in steam flooding process. However, the molecular composition understanding and contribution for oil production are still unclear. In this study, the composition analysis of the heavy oil was investigated in the core scale steam flooding process with the temperature from 120 to 280 °C. The crude oil, produced oils and residual oils were characterized comprehensively by gas chromatography and high-resolution mass spectrometry. It is found that steam flooding preferentially extracts aromatics and remains more resins in the residual oil. Viscosity reduction is the dominant mechanism when steam is injected at a low temperature. Large molecular heteroatoms with high carbon number and high double bond equivalent (DBE) are eluted into the produced oil, while compounds with low carbon number and low DBE are remained in the residual oil. As the steam temperature rises, the increased distillation effect results in the extraction of light hydrocarbons from the residual oil to the produced oil. More small heteroatoms with low carbon number and low DBE enter into the produced oil, especially in the none water cut stage. The compositional difference of produced oils is characterized in DBE versus carbon number distribution of the N and O containing compound classes. This work uses a variety of composition analysis methods to clarify the steam flooding mechanism and provides a novel understanding of steam flooding mechanisms with various temperatures and production stages from the molecular perspective.

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1. Introduction

Crude oil is a complex mixture of saturates, aromatics, resins and asphaltenes which contains carbon, hydrogen, sulfur, nitrogen, oxygen, as well as metal elements. The total original oil in place (OOIP) of crude oil has been proved to be 126.7 billion tons in the world, more than 70% of which are heavy oil (Castro et al., 2011; Yang and Duhamel, 2015; Guo et al., 2016). As one of the most abundant oil resources, heavy oil is mainly distributed in Liaohe, Shengli, Henan, Xinjiang oil fields in China (Li et al., 2022; Zhai et al., 2022). The property of heavy oil is different due to factors

such as burial depth, reservoir condition and migration distance in different oil fields (Talebkeikhah et al., 2020). There are usually four distinct characteristics compared to conventional light oil: (1) Heavy oil is a pseudoplastic fluid at low temperature and shows the property of Newtonian fluid at high temperature (Bazyleva et al., 2010). (2) The viscosity of heavy oil decreases significantly with the increase of temperature (Volek and Pryor, 1972). (3) Heavy oil contains more large molecules of resins, asphaltenes and wax, which easily form three dimensional network space structure and increase flow resistance (Piroozian et al., 2021). (4) Heteroatoms and metal elements combine together by association, which increases the viscosity of heavy oil and makes it more difficult to develop (Wang et al., 2021).

The primary method of heavy oil development technology is thermal recovery, which includes hot water flooding, steam huff and puff, steam flooding, steam-assisted gravity drainage (SAGD)

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and fire flooding (Luo and Gu, 2007; Mohammadzadeh et al., 2010; Zhao et al., 2014). Steam flooding has become one of the most widely used technologies to enhance oil recovery during the later phase in heavy oil reservoirs (Butler, 1994; Sun et al., 2017a, 2017b). Compared with water flooding, the oil production by steam injection in heavy oil reservoir was found to be greater at an equivalent temperature (Willman et al., 1961). Lots of physical experiments and numerical simulation have been conducted to study the mechanism of increasing oil production during steam flooding process (Neuman, 1985; Babadagli and Al-Bemani, 2007; Huang et al., 2018; He et al., 2022). Thermal viscosity reduction and steam distillation effect are the major mechanisms by injecting steam or gas-assisted steam into heavy oil (Willman et al., 1961). At the same time, a certain degree of aquathermolysis reaction occurs between heavy oil and high temperature steam (Yi et al., 2009; Montgomery et al., 2013). Otherwise, some other mechanisms have also been investigated by injecting multiple thermal fluid assisted steam, such as wettability alteration, interfacial tension (IFT) reduction, foaming effect, and emulsification (Huang et al., 2018; Liu et al., 2019; Pei et al., 2022; Pratama and Babadagli, 2022).

Compared with water flooding, the main mechanism of steam flooding is distillation effect, which has been studied for a long time (Volek and Pryor, 1972; Duerksen and Hsueh, 1983). The distillation effect was demonstrated to enhance heavy oil recovery by about 5%–10%. A lot of experimental studies have investigated the factors influencing the distillation rate during the steam injection process. Light components of heavy oil are distilled by the continuous steam injection at high temperature, and condensed into a liquid phase when contacting with cold heavy oil and rock at the boundary of the steam chamber. Heated oil of viscosity reduction together with the condensed oil components eventually improve the oil recovery. Distillation effect are greatly affected by the composition of heavy oil, the pressure and temperature of the injected steam (Liu et al., 2018). Kirmani et al. (2021) indicated that the high temperature with moderate quality of steam could enhance oil recovery in an economical way. Richardson et al. (2000) concludes that steam distillation causes large changes of viscosity, molecular weight, and composition by comparing the residual oil and original oil in Kern River oil. Superheated steam played a more effective role than saturated steam in heavy oil recovery. Vafaei et al. (2009) proposed that the temperature of steam and the mass fraction of lightweight components in heavy oil were the most important parameters with the distillation effect. The light weight and middle weight components of heavy oil could be completely extracted by distillation effect, which ultimately changed the composition of the residual oil.

In steam flooding heavy oil process, the high temperature steam destroys the balance of heavy oil component system, resulting in changes in the composition and properties of heavy oil, which must be considered in the subsequent development technology. However, heavy oil was always considered as a substance of constant composition in the research of enhanced oil recovery in steam flooding. And for steam flooding mechanisms, the studies on distillation effect were mainly concentrated in the reactor, but lack of research in porous media. Previous studies did not present a molecular composition understanding of EOR mechanism during steam flooding process.

In this paper, core scale steam flooding experiments of a heavy oil were carried out at different temperatures. The crude oil, produced oils and residual oils were characterized by gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS), high temperature simulated distillation (SIMDIS) and Orbitrap high-resolution MS. The composition analysis in steam flooding process was studied to clarify the dominant mechanism at different temperatures and dryness.

2. Materials and experiments

2.1. Materials

A heavy oil from Liaohe Oilfield in China was used in core steam flooding experiments. The heavy oil has a viscosity of 7128 mPa s at 60 °C (reservoir temperature) and 2.5 MPa (reservoir pressure). The experimental water was field filtered formation water with a salinity of 200 mg/L. Artificial sandstone cores with length of 30 cm × width of 4.5 cm × height of 4.5 cm, porosity of 27% and permeability of 4000 mD were used to simulate porous media.

2.2. Core steam flooding experiment

The experimental parameters were set to be the same as the actual reservoir conditions. A total of three core flooding experiments were conducted with steam injection temperatures of 120, 200 and 280 °C. The experimental parameters are shown in Table 1. The core was loaded into the high-temperature resistant core holder and then measured for permeability, vacuumed, saturated with the experimental water. The heavy oil was continuously injected by the plunger pump (Teledyne Isco 100DX, USA, 0–30 MPa) with the velocity ranging from 0.3 to 2 mL/min to create the irreducible water saturation and initial oil saturation. The core holder was put in thermostat which was set at reservoir temperature (60 °C) for 48 h of aging. The distilled water was pumped into the steam generator (Norbest Machinery Manufacturing Co. Ltd., China, 0–350 °C) and heated at the experimental temperature to form a stable steam. The dryness of steam is 70%–80% before it is injected into the core at 5 mL/min. The produced liquid was collected in test tubes at certain intervals and the injection pressure was recorded by the pressure sensor. Experiments were ended when the water cut reached 98% or steam channeling happened. Back pressure of 0.5 MPa was set at the outlet of core holder to prevent steaming during the whole steam flooding process. The volumes of oil and water were read respectively after they were separated completely. Fig. 1 shows the schematic diagram for the steam flooding experiment.

The oil in test tubes was collected in sampling bottles and denoted as “produced oil”. In the process of steam flooding, produced oils can be divided into two stages according to different water cut: none water cut ($fw = 0$) and high water cut ($fw > 0$). After steam flooding experiments, the remaining cores were subjected to Soxhlet extraction by trichloromethane for 72 h. The solvent in the extract collected was evaporated in a rotary evaporator. The extracted oil was collected in sampling bottles and denoted as “residual oil”.

2.3. SARA fractionation

The crude oil, produced oils and residual oils were first dehydrated in a vacuum drying oven (110 °C, 0.08 MPa of vacuum) before being separated into saturates, aromatics, resins, and asphaltenes (SARA) in accordance with ASTM D2007–19 method which is equivalent to Chinese industry standard NB/SH/T 0509–2010.

About 1 g of oil sample was briefly dissolved in 50 mL of *n*-heptane. The mixture was brought to a heating reflux for 1 h, cooled, and then was kept in dark for 2 h. The *n*-heptane precipitation was obtained by using a quantitative filter paper (medium speed) for the filtration process. The filter paper with precipitation was put into the extractor, and it was heated to reflux by using an *n*-heptane mixture for 1 h until the solvent was colorless. The *n*-heptane soluble fraction called maltene was obtained by vacuum rotary evaporation of the *n*-heptane mixture. By using 30 mL of

Table 1
Experimental parameters for the steam flooding experiments.

Number	Steam temperature, °C	Porosity, %	Permeability, mDa	Original oil saturation, %
1	120	29.87	4002	91.30
2	200	24.83	4124	91.47
3	280	28.30	4046	91.44

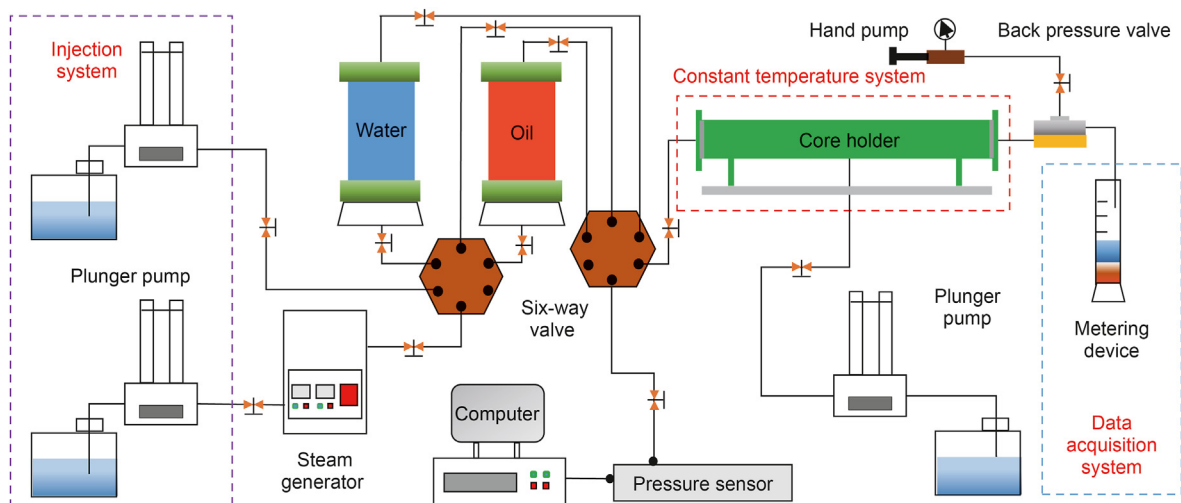


Fig. 1. Schematic diagram of the steam flooding experiment system.

toluene, the filter paper with precipitation in the extractor was heated to reflux for 1 h until the solvent was colorless. Asphaltenes were obtained by vacuum rotary evaporation of the toluene mixture. Maltene in *n*-heptane was concentrated to a volume of about 10 mL by vacuum rotary evaporation. Then maltene was fractionated into saturates, aromatics, and resins by alumina (100–200 mesh, activated at 500 °C for 6 h, with 1 wt% water added) column chromatography in a 50 °C circulating water bath. 80 mL of *n*-heptane and 80 mL of toluene were used to elute saturates and aromatics, respectively. Resins were eluted with 40 mL of toluene/ethanol (1:1, v:v), 40 mL of toluene and 40 mL of ethanol. The solvent in each effluent was dried by vacuum drying oven (110 °C, 0.08 MPa of vacuum) and weighed repeatedly until it reached a constant weight after cooling.

2.4. Simulated distillation

The high-temperature simulated distillation analysis was conducted with a modified Agilent 6890N GC system (Analytical Controls, Netherland). An AC HT-750 High-temperature column (5 m × 0.53 mm internal diameter × 0.18 μm film thickness) was used to analyze boiling point ranges of the crude oil, produced oils and residual oils. The oven was held at 40 °C for 1 min, ramped up to 430 °C at 10 °C/min, and then held at 430 °C for 5 min. The carrier gas, helium, was invoked at a flow rate of 19 mL/min. The injector was kept at 100 °C for 15 min, heated up to 430 °C at 15 °C/min, and then maintained at 430 °C for 22 min. The flame ionization detector (FID) was maintained at 430 °C. The volume of the sample injection was set at 1 μL.

2.5. GC-FID

The hydrocarbon of the crude oil, produced oils and residual oils was analyzed by using an Agilent 7890A GC combined with a flame ionization detector (FID). A HP-1 elastic silica capillary column

(60 m × 0.25 mm internal diameter × 0.25 μm film thickness) was employed in GC-FID. The oven was held at 40 °C for 10 min, ramped up to 70 °C at 4 °C/min, ramped from 70 to 310 °C at 8 °C/min, and then maintained at 310 °C for 40 min. Both of the injector and the FID were kept at 310 °C. Nitrogen was used as the carrier gas with a flow rate of 1 mL/min. Split ratio was set to 20:1.

2.6. GC-MS

An Agilent 7890A GC coupled with a 5975C mass spectrometer was used to analyze the saturates by using a HP-5 fused silica capillary column (60 m × 0.25 mm internal diameter × 0.25 μm film thickness). The column was initially held at 50 °C for 1 min, ramped up to 120 °C at 20 °C/min, ramped from 120 to 250 °C at 4 °C/min, ramped from 250 to 310 °C at 3 °C/min, and finally maintained at 310 °C for 30 min. The injector and transfer line were both maintained at 300 °C. The carrier gas, helium, was used at a flow rate of 1 mL/min. The MS ion source, which was maintained at a constant temperature of 250 °C, was operated in the electron-impact ionization (EI) mode with an electron beam energy of 70 eV. The mass range was set to m/z 35–600.

2.7. Orbitrap MS

An Orbitrap Fusion MS (Thermo Scientific) combined with ESI source was used to analyze polar compounds in the crude oil, produced oils and residual oils. About 10 mg oil sample was dissolved in 1 mL of toluene, and then 20 μL of toluene solution was diluted with 1 mL of toluene/methanol (1:3, v:v) for Orbitrap MS analysis with direct injection. The sample was injected into the ESI source at a rate of 6 μL/min by using a mini pump. All samples were analyzed in negative ion mode with 2600 V ion spray voltage. Sheath gas flow rate and auxiliary gas flow rate were set to 5.0 Arb and 2.0 Arb, respectively. Additionally, the ion transfer tube and vaporizer were adjusted to temperatures of 300 and 20 °C. The MS

resolution could reach to 550,000 at m/z 150. Each mass spectrum was detected in 1.5 min with a mass range of m/z 150–800. Data analysis was performed by Thermo Xcalibur Qual Browser. The compound assignment was carried out by using a home built software which has been described elsewhere (Liu et al., 2011; Shi et al., 2013).

3. Results and discussion

3.1. Steam flooding result and SARA composition

The recovery is defined as the ratio of cumulative oil production to original oil in core. The water cut is defined as the ratio of water production to liquid production. The recovery and water cut curves of steam flooding are presented in Fig. 2(a). The recovery of steam injected at 120, 200 and 280 °C were 36.4%, 40.7% and 28.9%, respectively. Compared steam flooding at 120 °C, the oil recovery exhibited a 4.3% increase at 200 °C and a 7.5% decrease at 280 °C. With the increase of steam temperature, no steam was produced in the experiment at 120 and 200 °C, while a large amount of steam was observed when steam was injected at 280 °C. The water breakthrough time was extended with the increase of temperature. In high water cut stage, the water cut curves are basically the same at different temperatures. Fluctuations occur when water cut reaches 80%. In the steam flooding process, steam is expanding and the heavy oil is heated from injection to production end of the core constantly. Steam condenses into hot water when it contacts cold heavy oil and rock. Heavy oil, hot water, and steam move alternately through the formation, causing emulsification and water cut fluctuations. The fluctuation of water cut can be regarded as the feature in high water cut stage of steam flooding heavy oil.

As shown in Fig. 2(b), the higher the steam temperature, the lower the pressure at the beginning of the experiment. The increase of steam temperature can reduce the starting pressure of heavy oil in steam flooding process. An increase in the temperature generates a decrease in the viscosity of the heavy oil and an improvement of the oil-water mobility ratio, which contributes to the prolong of the water-free recovery stage and the increase of the oil recovery. The pressure increases first and then decreases in steam flooding process, but the decreasing range of pressure difference decreases with the increase of temperature. Heavy oil which has a low viscosity is more likely to emulsify with steam. At the same time, the higher the steam temperature, the larger the dryness of steam. The dryness of the injected steam entering the core can be calculated during steam flooding process at 120, 200 and 280 °C. The dryness of the injected steam at the highest pressure of the experiment is 10%, 100% and over 100%. The steam in the core is remained in unsaturated, saturated and superheated state, respectively. The increase of dryness promotes the enhancement of distillation effect and further leads to the emulsification more easily. The viscosity of

produced emulsions and oils increases continuously under emulsification, which could increase the seepage resistance and the pressure difference in steam flooding process.

The SARA composition of the crude oil, produced oils and residual oils are listed in Table 2. The total yield of heavy oil is less than 100% because of the loss of light components in saturates and aromatics during separation process. The relative contents of saturates and resins in produced oils are decreased and the relative contents of aromatics and asphaltenes gradually increase compared with the raw crude oil at different temperature conditions. In the process of steam flooding heavy oil at 120 °C, compared with produced oils in none water cut stage ($fw = 0$), the resins content of heavy oils in high water cut stage ($fw > 0$) increase and the other three fractions decrease. However, with the temperature of steam increase to 200 and 280 °C, the resins content of heavy oils decreases and the other three fractions increase. High temperature steam could result in higher asphaltene contents and lower resin content in steam flooding heavy oil. As a higher content component in heavy oil, resins are converted to saturates and aromatics by aquathermolysis reaction (Yi et al., 2009; Montgomery et al., 2013; Liu et al., 2018). The SARA composition changes of residual oils are opposite to that of produced oils. The relative contents of resins in residue oils increase significantly and the other three fractions decrease from crude oil to produced oils. With the increase of temperature, the relative contents of saturates and asphaltenes in residual oils decrease and the relative contents of aromatics and resins increase. Saturates decrease in both produced and residual oils because light saturates are relatively removed partly in the distillation process at high temperature.

The steam injected at 120 °C is mainly used for viscosity reduction rather than distillation in porous rocks. Due to the small steam temperature difference with the formation temperature, the steam condenses easily into water in flooding process which is almost like hot water flooding. Because of the high solubility of small molecule aromatics in water, the relative contents of aromatics in high water cut stage ($fw > 0$) produced oils decrease compared with none water cut stage ($fw = 0$). With the increase of temperature, the enhanced distillation effect causes hot water flooding turn into water-steam flooding or steam flooding. Therefore, in the process of steam flooding at 200 and 280 °C, the change of aromatics content in produced oils from none water cut stage ($fw = 0$) to high water cut stage ($fw > 0$) produced oils is opposite compared with 120 °C. At the same time, the increase of resins content in residual oils with the increase of steam temperature is also a proof of the enhanced distillation effect.

3.2. Hydrocarbons analysis by GC and GC-MS

Fig. 3 shows GC chromatograms of the crude oil, produced oils and residual oils. The crude oil is a severely biodegraded one with

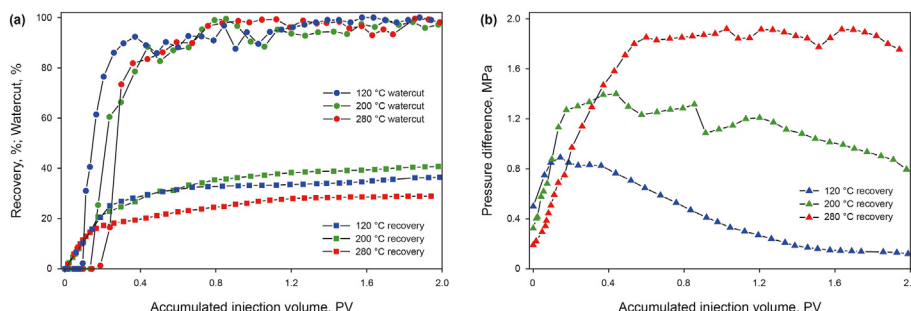


Fig. 2. Recovery, water cut (a) and pressure difference (b) curves as function of accumulated injection volume during steam flooding process.

Table 2
SARA composition of the crude oil, produced oils and residual oils.

Sample	Saturates, wt%	Aromatics, wt%	Resins, wt%	Asphaltenes, wt%
Crude oil	20.74	35.59	30.06	14.39
120 °C <i>fw</i> = 0	20.35	39.80	24.06	15.51
120 °C <i>fw</i> > 0	15.22	37.87	28.09	14.43
120 °C Residual	16.04	31.75	38.30	13.91
200 °C <i>fw</i> = 0	14.20	35.93	28.37	16.25
200 °C <i>fw</i> > 0	16.09	38.45	26.71	16.47
200 °C Residual	13.51	32.64	39.15	13.70
280 °C <i>fw</i> = 0	16.80	38.61	28.25	15.93
280 °C <i>fw</i> > 0	18.51	39.45	27.61	15.03
280 °C Residual	11.28	32.94	43.18	12.59

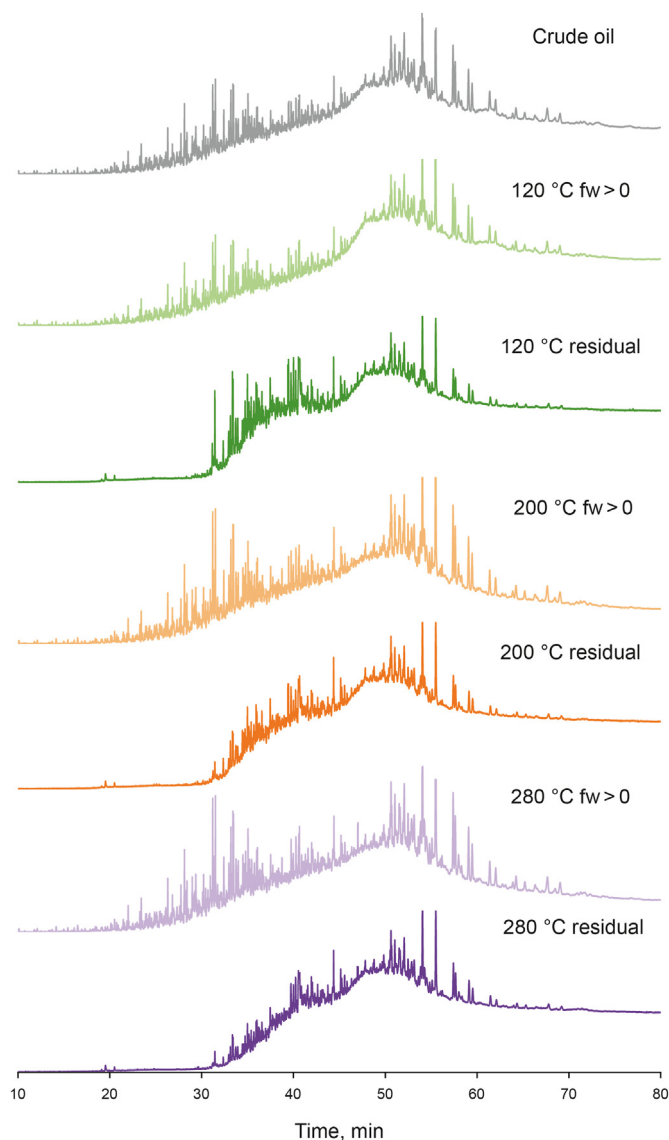


Fig. 3. GC chromatograms of the crude oil, produced oils and residual oils.

large amounts of naphthenes according to the chromatogram. With the increase of steam temperature, the intensity of peaks before 40 min of produced oils gradually increases and that of residual oils decreases compared with the crude oil. There is no peak before 30 min of residual oils because small hydrocarbons are extracted into produced oils or lost into steam, which also corresponds to the

increasing of initial boiling point on the basis of the high temperature simulation distillation. The composition change of heavy oil in water flooding process has been studied in our previous research, the hydrocarbons in produced oils is generally not affected by temperature based on GC analysis (Zhang et al., 2022). Therefore, the increase of relative abundance of small hydrocarbons in produced oils is mainly due to the distillation effect in steam flooding process. The temperature difference between the injected steam and the experimental temperature is small at 120 °C. Steam is easy to condense, causing more small molecular hydrocarbons enter into residual oils. With the steam temperature increase to 200 and 280 °C, distillation effect is enhanced and condensation effect is decreased. Small molecular hydrocarbons are condensed into produced oils, which is an important enhanced oil recovery mechanism of steam flooding process.

The saturates of the heavy oil which characterized by GC-MS are mainly made up of *n*-alkanes, bicyclic terpanes, tricyclic terpanes, steranes and hopanes. Selected peaks were identified based on retention time and integral calculated based on heights and abundance. Fig. 4 gives the integral area ratio of *n*-alkanes/bicyclic terpanes (a), *n*-alkanes/tricyclic terpanes (b), bicyclic/tricyclic terpanes (c) and steranes/hopanes (d), which can equal to the relative content ratio approximately. The area ratio of *n*-alkanes/bicyclic terpanes in produced oils increase and the area ratio of *n*-alkanes/tricyclic terpanes, bicyclic/tricyclic terpanes decrease and steranes/hopanes stays basically compared with the raw crude oil at different temperature conditions. In the process of steam flooding heavy oil at 120 °C, compared with produced oils in none water cut stage (*fw* = 0), the area ratios of *n*-alkanes/tricyclic terpanes and bicyclic/tricyclic terpanes in high water cut stage (*fw* > 0) decrease and bicyclic/tricyclic terpanes increase. However, with the temperature of steam increase to 200 and 280 °C, the area ratios of *n*-alkanes/tricyclic terpanes and bicyclic/tricyclic terpanes in high water cut stage (*fw* > 0) increase and bicyclic/tricyclic terpanes decrease. The area ratios of *n*-alkanes/bicyclic terpanes and *n*-alkanes/tricyclic terpanes in residual oils change significantly and identically which is shown in Fig. 4(a) and (b). In steam flooding heavy oil process, the area ratios at 120 °C are 1.99 and 1.65 respectively which are the highest. However, the area ratios decrease significantly to 0.83 and 1.13 with the temperature of steam increase to 200 °C and increase slightly to 1.25 and 1.61 at 280 °C. As shown in Fig. 4(c), the area ratio of bicyclic/tricyclic terpanes at 120 °C is 0.83 and increase to 1.37 at 200 °C and 1.29 at 280 °C respectively. The area ratio of steranes/hopanes stays the same basically from 120 to 280 °C which is shown in Fig. 4(d).

The variation which is similar to the change of SARA composition at different temperatures is also mainly due to the different solubility of saturates in water and steam. The solubility of naphthenes decreases with the increase of temperature and ring number. The solubility of bicyclic and tricyclic terpanes in water is higher than that of *n*-alkanes and the solubility of bicyclic terpanes

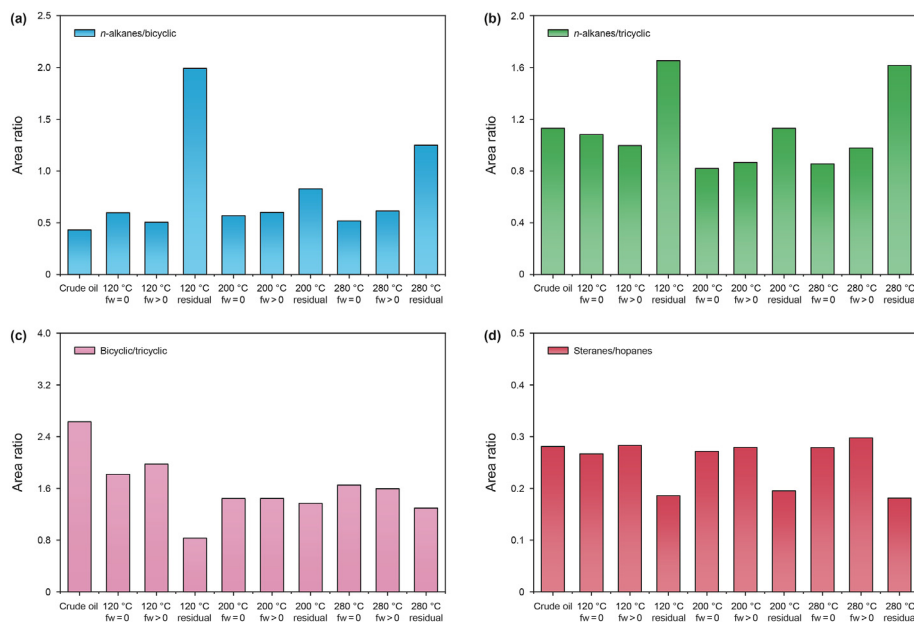


Fig. 4. Integral area ratio of *n*-alkanes/bicyclic terpanes (a), *n*-alkanes/tricyclic terpanes (b), bicyclic/tricyclic terpanes (c) and steranes/hopanes (d) of the crude oil, produced oils and residual oils by GC-MS.

is higher than that of tricyclic terpanes. Therefore, the area ratio of *n*-alkanes/bicyclic terpanes and *n*-alkanes/tricyclic terpanes is highest and bicyclic/tricyclic terpanes is lowest in the process of steam flooding heavy oil at 120 °C. With the steam temperature increase to 200 °C, the enhanced distillation effect causes the reduced solubility of saturates in steam. Therefore, the area ratio of *n*-alkanes/bicyclic terpanes and *n*-alkanes/tricyclic terpanes decrease and bicyclic/tricyclic terpanes increase. The lowest area ratio represents the highest relative content of naphthenes in the process of water-steam flooding heavy oil at 200 °C. However, some large hydrocarbon compounds such as terpanes crack into small molecular compounds at 280 °C. So the relative content of *n*-alkanes in residual oils at 280 °C is higher than 200 °C.

3.3. Boiling point ranges of heavy oil

Simulated distillation (SIMDIS) is a GC method to simulate the atmospheric distillation of oil components, which is expressed in terms of oil yield as a function of true boiling points of petroleum fractions (Ni et al., 2015). The simulated distillation curves of the crude oil (a), produced oils in none water cut stage (b), produced oils in high water cut stage (c) and residual oils (d) are shown in Fig. 5. The initial boiling point (IBP) of the crude oil is 184 °C. and the final yield is 82.2%. As the upper limit of operating temperature of most GC columns (300 °C), 36.2% of oil components is obtained at 500 °C and has been discussed in this paper. In other words, 47.6% of the heavy oil cannot be detected through column in a typical GC or GC-MS analysis. Therefore, the high temperature simulated distillation is usually used to analyze heavy oil because of its ability to detect oil components below boiling points of 750 °C.

With the increase of temperature, the produced oils in none water cut stage ($fw = 0$) become lighter with the final yields increase from 84.5% to 99.5%, and the produced oils in high water cut stage ($fw > 0$) become heavier with the final yields decrease from 91.7% to 83.8%. The yields from 500 to 750 °C of produced oils in none water cut stage ($fw = 0$) increase from 49.7% to 62.4%. The yields from 500 to 750 °C of produced oils in high water cut stage ($fw > 0$) decrease from 55% to 47.9%. All produced oils contain more

heavy fractions, leading to higher distillation yields than that of the crude oil. Distillation has a higher effect on heavy components during steam flooding process, especially in none water cut stage ($fw = 0$). The boiling points curves of residual oils are opposite but different to that of produced oils. As shown in Fig. 5(d), the initial boiling point (IBP) of the residual oil is about 280–305 °C, which is higher than the crude oil and produced oils. All the residual oils have large amounts of light components with 100% yields. With the increase of temperature, the yields below 500 °C of residual oils decrease from 42.2% to 36%. Although distillation effect is enhanced with steam temperature increases from 120 to 280 °C, the residual oil at 200 °C has 20.8% of components with boiling point below 400 °C, which is higher than that at 120 °C (16.7%) and at 280 °C (12.8%).

When steam is injected at 120 °C, the viscosity of crude oil decreases by 95.1%. The viscosity of crude oil turns from 7603 mPa s to 372 mPa s. Viscosity reduction is the main mechanism when steam is injected at a low temperature, thermal effect influences light components into produced oils. When steam temperature increases to the initial boiling point (184 °C), the viscosity of crude oil turns to 192 mPa s. When the temperature continues to rise, the oil viscosity changes little and the viscosity reduction reached a limit. The increase of distillation effect enhances the extraction of heavy components, which is also an important reason to enhance oil recovery for heavy oil. The composition changes of produced oils in none water cut stage ($fw = 0$) and high water cut stage ($fw > 0$) become more visible, which may be a reason for the reduced recovery at high temperature.

3.4. Heteroatoms analysis by orbitrap MS

Fig. 6 shows the relative abundance of compound classes assigned from negative-ion ESI Orbitrap mass spectra of the crude oil, produced oils and residual oils. There were 14 compound classes detected which N1 and O2 classes were dominant in the negative-ion ESI Orbitrap mass spectra. According to the previous studies, negative-ion ESI has been successfully used to analyze heteroatoms in heavy oil (Shi et al., 2013). The N1, O1 and O2 class

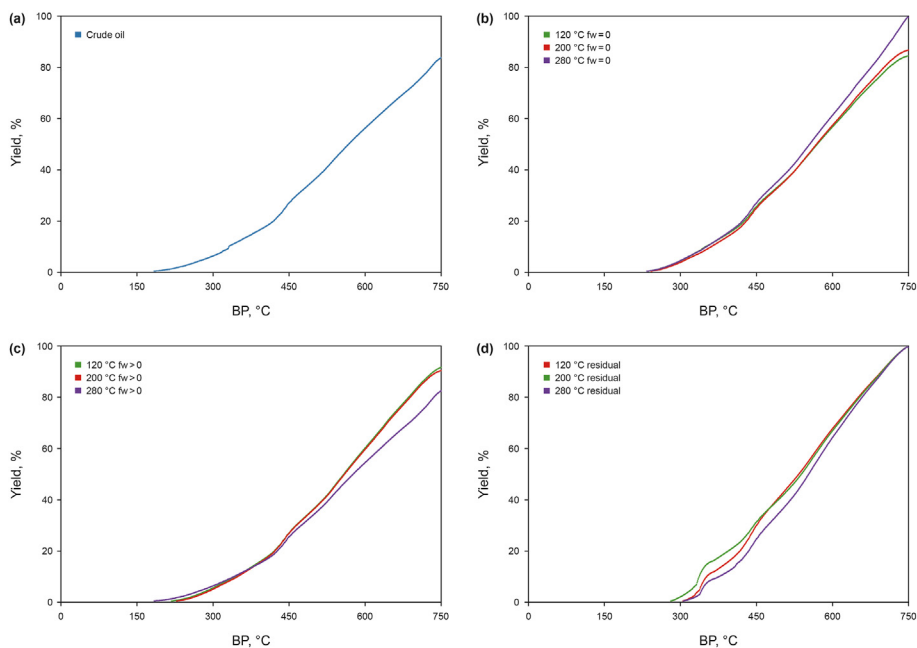


Fig. 5. Simulated distillation curves of the crude oil (a), produced oils in none water cut stage (b), produced oils in high water cut stage (c) and residual oils (d).

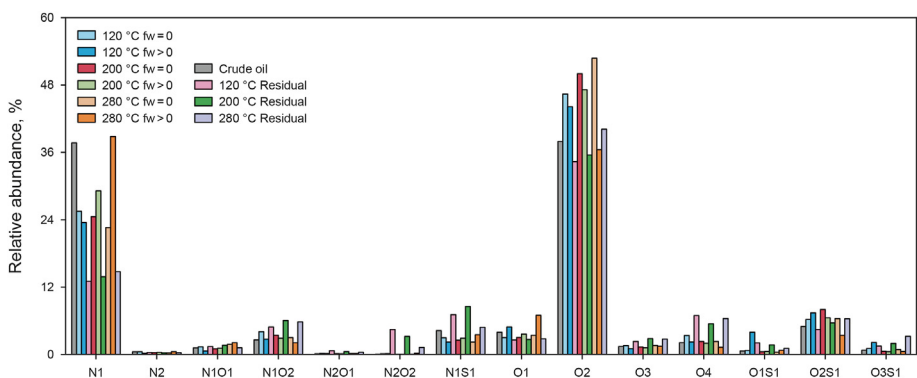


Fig. 6. Relative abundance of compound classes assigned from negative-ion ESI Orbitrap mass spectra of the crude oil, produced oils and residual oils.

detected in negative-ion ESI are neutral nitrogen compounds (carbazoles, benzocarbazoles, dibenzocarbazoles), phenols and carboxylic acids, respectively. Compared with the crude oil, the relative abundance of N1 class in produced oils is lower than 37.7%, while the relative abundance of O2 class is higher than 37.9% obviously. With the increase of temperature, the relative abundance of N1 class in produced oils of none water cut stage ($fw = 0$) decrease from 25.5% to 22.6% and the relative abundance of O2 class increase from 46.4% to 52.8%. However, the relative abundance of N1 class in produced oils of high water cut stage ($fw > 0$) increase, while the relative abundance of O2 class increase from 120 to 200 °C and decrease significantly at 280 °C. Molecular selectivity for heteroatoms in heavy oil is different during steam flooding process and increases with increasing temperature. Carboxylic acids (O2 class) are preferred to be extracted into produced oils in none water cut stage ($fw = 0$) and neutral nitrogen compounds (N1 class) in high water cut stage ($fw > 0$). Compared with the crude oil and produced oils, the residual oils have relatively higher abundances in classes containing multiple heteroatoms such as O3, O4, N1O1, N1O2, N2O1, N2O2 and N1S1 classes. The results showed that classes containing multiple heteroatoms are more difficult to be

extracted into produced oils by steam flooding.

Compared to the results of the crude oil, the plots of double bond equivalent (DBE) as a function of carbon number for produced oils and residual oils are significantly different which are shown in Fig. 7. The dot size corresponds to the relative abundance of the component, normalized by the total abundance of each class. The distribution of carbon number and DBE in crude oil, produced oils and residual oils is generally the same, but the relative abundance distribution centers are different. The average carbon number and DBE of different classes have been listed in Table 3. In the process of steam flooding heavy oil at 120 °C, the relative abundance distribution centers for heteroatoms of produced oils both in none water cut stage ($fw = 0$) and high water cut stage ($fw > 0$) move to high carbon number and high DBE compared with the crude oil. The average carbon number and DBE of each compound class in produced oils of high water cut stage ($fw > 0$) are higher than that in produced oils of none water cut stage ($fw = 0$). When temperature increase to 200 and 280 °C, the relative abundance distribution centers move to low carbon number and low DBE, especially for N1O1 and N1O2 classes. The average carbon number of each compound class in produced oils of the same steam flooding stage

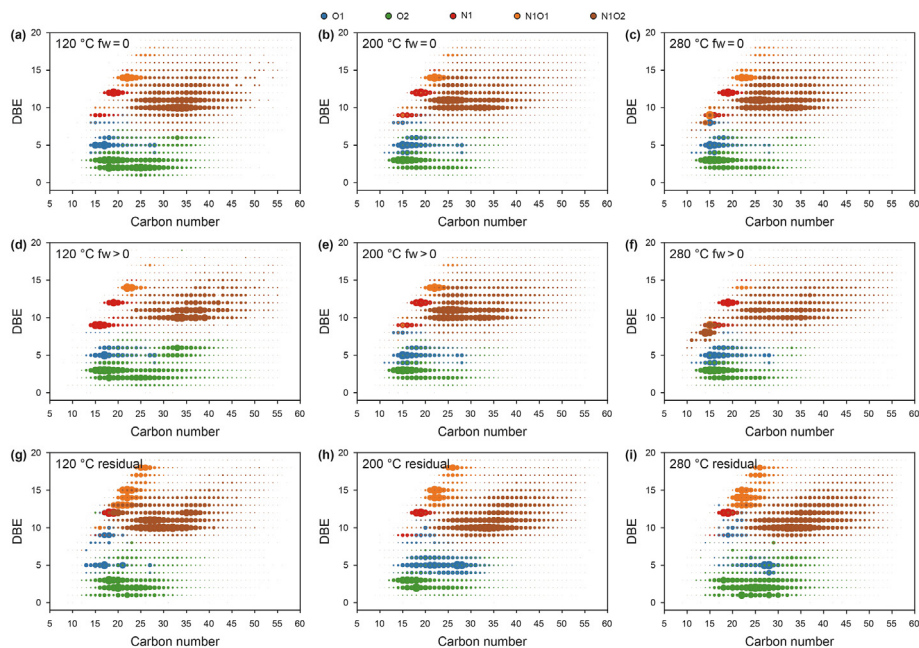


Fig. 7. Relative abundance distribution plots of DBE versus carbon number of O1, O2, N1, N1O1 and N1O2 class in the crude oil and produced oils and residual oils.

Table 3

Average carbon number and DBE of O1, O2, N1, N1O1 and N1O2 class in the crude oil and produced oils and residual oils.

Sample	O1		O2		N1		N1O1		N1O2	
	CN	DBE	CN	DBE	CN	DBE	CN	DBE	CN	DBE
Crude oil	23.8	6.3	22.6	3.9	23.1	11.7	25.4	13.1	32.0	11.5
120 °C fw = 0	24.7	6.5	26.6	4.0	23.9	11.9	26.5	13.7	34.7	11.7
120 °C fw > 0	24.8	7.3	28.6	4.4	25.2	11.4	30.9	13.9	37.3	11.9
120 °C Residual	20.0	6.8	24.9	4.0	21.6	12.0	24.2	14.6	32.7	12.2
200 °C fw = 0	23.0	7.1	23.2	4.1	22.9	11.6	25.6	13.4	32.9	11.8
200 °C fw > 0	22.8	6.9	22.8	4.2	22.7	11.5	25.4	13.3	32.6	11.7
200 °C Residual	24.4	6.9	25.0	4.0	23.2	12.5	26.4	14.9	36.1	12.1
280 °C fw = 0	22.7	7.1	23.0	4.1	23.3	11.5	24.7	13.2	32.3	11.7
280 °C fw > 0	22.0	7.0	22.6	4.1	22.7	11.4	24.0	12.3	32.1	11.4
280 °C Residual	24.9	8.1	28.1	4.0	23.3	12.6	26.4	15.1	36.8	12.0

decrease with the temperature increase. However, the relative abundance distribution centers of residual oils are opposite to that of produced oils. In the process of steam flooding heavy oil at 120 °C, the relative abundance distribution centers of DBE versus carbon number for heteroatoms in residual oils move to lower carbon number and high DBE compared with that in produced oils. And with temperature increase to 200 and 280 °C, the relative abundance distribution centers of DBE versus carbon number for heteroatoms in residual oils move to high carbon number and high DBE. The average carbon number of each compound class in residual oils increase with the temperature increase.

Under the thermal effect of hot water flooding at 120 °C, the viscosity of heavy oil decreases greatly in the sweep volume of water. Large compounds with high carbon number and high DBE enter into produced oils, while strong polar small compounds with low carbon number and low DBE are remained in residual oils. With steam temperature increase, steam keeps in touch with heavy oil in cores and distillation effect enhance, causing low carbon number with low DBE compounds which is close to the crude oil enter into produced oils. More large compounds with high carbon number and high DBE are remained in residual oils.

3.5. Property discussion for produced emulsion and oil

The higher the steam temperature, the increase of dryness during steam flooding process. The temperature and dryness of steam lead to the mechanism difference such as viscosity reduction and distillation effect, which will also lead to physical properties changes of the crude oil and produced oils. The viscosity of produced emulsion and oil was measured at 60 °C, which is shown in Fig. 8. Emulsification is a common phenomenon in steam flooding process, causing a higher viscosity of produced emulsions than that of produced oils. With the increase of steam temperature, the viscosity of produced emulsions and oils in none water cut stage ($fw = 0$) increases continuously. The viscosity of produced emulsions in high water cut stage ($fw > 0$) increases from 9020 mPa s to 13,330 mPa s, but the viscosity of produced oils increases from 8287 mPa s to 10,760 mPa s and then decreases to 7570 mPa s. The viscosity difference between produced emulsion and oil becomes larger with the increase of temperature.

The molecular selectivity for hydrocarbons and heteroatoms can explain why viscosity of produced oils varies differently in steam flooding heavy oil process. With the increase of temperature, the viscosity of produced emulsions and oils in none water cut stage ($fw = 0$) increases due to the extraction of heavy components and carboxylic acids. In high water cut stage ($fw > 0$), W/O emulsion formation also increases the viscosity of produced emulsions. However, as the temperature rising to 280 °C, more light hydrocarbons and small molecular heteroatoms are eluted into produced oils by distillation effect, which greatly reduce the viscosity of produced oils in high water cut stage ($fw > 0$). Because of the increase of light components in produced oils, the viscosity of the produced oil in high water cut stage is obviously lower than that in none water cut stage, resulting in the steam channeling phenomenon. At the same time, a lower content of carboxylic acids may decrease emulsification, resulting in a lower viscosity of produced emulsion. The significant difference in viscosity lead to a steam channeling problem and a lower oil recovery easily. The viscosity and compositional changes of produced emulsions and oils can not only provide some experience on emulsifying phenomenon of

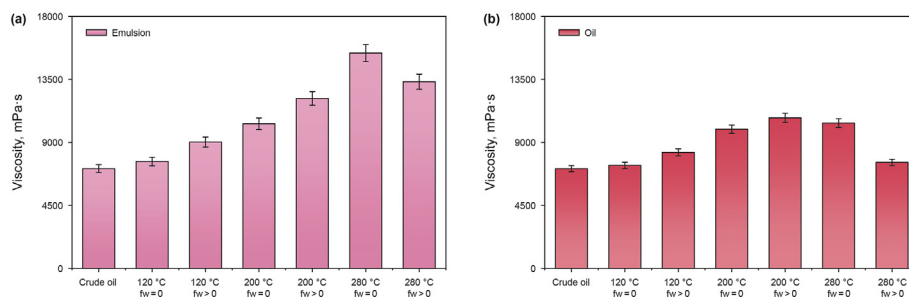


Fig. 8. The viscosity of the produced emulsion (a) and oil (b) at different temperatures.

heavy oil, but also explain enhanced oil recovery mechanism in the development of oilfield.

4. Conclusions

The enhanced oil recovery mechanism of steam flooding was investigated by analyzing the molecular composition of the crude oil, produced oils and residual oils. When steam is injected at different temperature and dryness, steam flooding mechanism has different influence on components of the heavy oil.

Steam preferentially extracts aromatics and remains more resins in the residual oil. When steam is injected at a low temperature, viscosity reduction causes light hydrocarbons into the residual oil. Large molecular heteroatoms with high carbon number and high DBE are eluted into the produced oil, while strong polar small compounds with low carbon number and low DBE are remained in the residual oil. As the steam temperature rises, the increased distillation effect results in the extraction of light hydrocarbons from the residual oil to the produced oil. Heteroatoms with low carbon number and low DBE are eluted into the produced oil. More large molecular heteroatoms with high carbon number and high DBE are remained in residual oils. Furthermore, the composition changes of produced oils from different steam flooding stages become more visible.

This study gives a better understanding for steam flooding mechanisms. The molecular composition of the residual oil can be inferred based on temperature field distribution and provide the technical direction to further enhance oil recovery such as multiple thermal fluids method. The result can also be used to build GEM model in numerical simulation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

Babadagli, T., Al-Bemani, A., 2007. Investigations on matrix recovery during steam injection into heavy-oil containing carbonate rocks. *J. Petrol. Sci. Eng.* 58 (7), 259–274. <https://doi.org/10.1016/j.petrol.2007.01.003>.

Bazyleva, A.B., Anwaru IHasan, M.D., Fulem, M., et al., 2010. Bitumen and heavy oil rheological properties: reconciliation with viscosity measurements. *J. Chem. Eng. Data* 55 (3), 1389–1397. <https://doi.org/10.1021/jc900562u>.

Butler, R.M., 1994. Steam-assisted gravity drainage: concept, development, performance and future. *J. Can. Petrol. Technol.* 33 (2), 44–50. <https://doi.org/10.2118/94-02-05>.

Castro, L.V., Flores, E.A., Vazquez, F., 2011. Terpolymers as flow improvers for Mexican crude oils. *Energy Fuel* 25 (2), 539–544. <https://doi.org/10.1021/ef101074m>.

Duerksen, J.H., Hsueh, L., 1983. Steam distillation of crude oils. *Soc. Petrol. Eng. J.* 23 (2), 265–271. <https://doi.org/10.2118/10070-PA>.

Guo, K., Li, H.L., Yu, Z.X., 2016. In-situ heavy and extra-heavy oil recovery: a review.

Fuel 185, 886–902. <https://doi.org/10.1016/j.fuel.2016.08.047>.

He, H.F., Li, Q., Zheng, H.R., et al., 2022. Simulation and evaluation on enhanced oil recovery for steam huff and puff during the later phase in heavy oil reservoir—A case study of block G in Liaohe Oilfield, China. *J. Petrol. Sci. Eng.* 219, 111092. <https://doi.org/10.1016/j.petrol.2022.111092>.

Huang, S.J., Cao, M., Cheng, L.S., 2018. Experimental study on the mechanism of enhanced oil recovery by multi-thermal fluid in offshore heavy oil. *Int. J. Heat Mass Tran.* 122, 1074–1084. <https://doi.org/10.1016/j.jheatmasstransfer.2018.02.049>.

Kirman, F.U.D., Raza, A., Gholami, R., et al., 2021. Analyzing the effect of steam quality and injection temperature on the performance of steam flooding. *Energy Geoscience* 2 (1), 83–86. <https://doi.org/10.1016/j.engeos.2020.11.002>.

Li, L., Yang, J., Zou, X., et al., 2022. A new production string for improving the thermal recovery of offshore heavy oil in small block reservoirs. *J. Petrol. Sci. Eng.* 211, 110131. <https://doi.org/10.1016/j.petrol.2022.110131>.

Liu, P., Shi, Q., Pan, N., et al., 2011. Distribution of sulfides and thiophenic compounds in VGO subfractions: characterized by positive-ion electrospray Fourier transform ion cyclotron resonance mass spectrometry. *Energy Fuel* 25 (7), 3014–3020. <https://doi.org/10.1021/acs.iecr.9b02272>.

Liu, P.C., Yuan, Z., Zhang, S.F., et al., 2018. Experimental study of the steam distillation mechanism during the steam injection process for heavy oil recovery. *J. Petrol. Sci. Eng.* 166, 561–567. <https://doi.org/10.1016/j.petrol.2018.03.096>.

Liu, Z.Y., Mendiratta, S., Chen, X., et al., 2019. Amphiphilic-polymer-assisted hot water flooding toward viscous oil mobilization. *Ind. Eng. Chem. Res.* 58 (36), 16552–16564. <https://doi.org/10.1021/acs.iecr.9b02272>.

Luo, P., Gu, Y.A., 2007. Effects of asphaltene content on the heavy oil viscosity at different temperatures. *Fuel* 86 (7), 1069–1078. <https://doi.org/10.1016/j.fuel.2006.10.017>.

Mohammadzadeh, O., Rezaei, N., Chatzis, I., 2010. Pore-level investigation of heavy oil and bitumen recovery using solvent-aided steam assisted gravity drainage (SA-SAGD) process. *Energy Fuel* 24 (12), 6327–6345. <https://doi.org/10.1021/ef100621s>.

Montgomery, W., Court, R.W., Rees, A.C., et al., 2013. High temperature reactions of water with heavy oil and bitumen: insights into aquathermolysis chemistry during steam-assisted recovery. *Fuel* 113, 426–434. <https://doi.org/10.1016/j.fuel.2013.05.098>.

Neuman, C.H., 1985. A gravity override model of steamdrive. *J. Petrol. Technol.* 37 (1), 163–169. <https://doi.org/10.2118/13348-PA>.

Ni, H.X., Hsu, C.S., Lee, P., et al., 2015. Supercritical carbon dioxide extraction of petroleum on kieselguhr. *Fuel* 141, 74–81. <https://doi.org/10.1016/j.fuel.2014.09.126>.

Pei, H.H., Zheng, J.Z., Zhang, G.C., et al., 2022. Combination of nano-bentonite stabilized foam and ultra-low IFT surfactant additives assisted steam injection to enhanced heavy oil recovery. *J. Mol. Liq.* 368, 120647. <https://doi.org/10.1016/j.molliq.2022.120647>.

Piroozian, A., Hemmati, M., Safari, M., et al., 2021. A mechanistic understanding of the water-in-heavy oil emulsion viscosity variation: effect of asphaltene and wax migration. *Colloids Surf. A Physicochem. Eng. Asp.* 608, 125604. <https://doi.org/10.1016/j.colsurfa.2020.125604>.

Pratama, R.A., Babadagli, T., 2022. A review of the mechanics of heavy-oil recovery by steam injection with chemical additives. *J. Petrol. Sci. Eng.* 208, 109717. <https://doi.org/10.1016/j.petrol.2021.109717>.

Richardson, W.C., Beladi, M.K., Wu, C.H., 2000. Steam distillation studies for the Kern River field. *SPE Reservoir Eval. Eng.* 3 (1), 13–22. <https://doi.org/10.2118/60909-PA>.

Shi, Q., Pan, N., Long, H.Y., et al., 2013. Characterization of middle-temperature gasification coal tar. Part 3: molecular composition of acidic compounds. *Energy Fuel* 27 (1), 108–117. <https://doi.org/10.1021/ef301431y>.

Sun, F.R., Yao, Y.D., Chen, M.Q., et al., 2017a. Performance analysis of superheated steam injection for heavy oil recovery and modeling of wellbore heat efficiency. *Energy* 125, 795–804. <https://doi.org/10.1016/j.energy.2017.02.114>.

Sun, F.R., Yao, Y.D., Li, X.F., et al., 2017b. The flow and heat transfer characteristics of superheated steam in offshore wells and analysis of superheated steam performance. *Comput. Chem. Eng.* 100, 80–93. <https://doi.org/10.1016/j.compchemeng.2017.01.045>.

Talebkeikah, M., Nait Amar, M., Naseri, A., et al., 2020. Experimental measurement

- and compositional modeling of crude oil viscosity at reservoir conditions. *J. Taiwan Inst. Chem. Eng.* 109, 35–50. <https://doi.org/10.1016/j.jtice.2020.03.001>.
- Vafaei, M.T., Eslamloueyan, R., Enfeali, L., et al., 2009. Analysis and simulation of steam distillation mechanism during the steam injection process. *Energy Fuel*. 23 (1), 327–333. <https://doi.org/10.1021/ef800602w>.
- Volek, C.W., Pryor, J.A., 1972. Steam distillation drive-Brea Field, California. *J. Petrol. Technol.* 24 (8), 899–906. <https://doi.org/10.2118/3441-PA>.
- Wang, L.T., Hu, Y.Y., Wang, L.H., et al., 2021. Visbreaking of heavy oil with high metal and asphaltene content. *J. Anal. Appl. Pyrol.* 159, 105336. <https://doi.org/10.1016/j.jaap.2021.105336>.
- Willman, B.T., Valleroy, V.V., Runberg, G.W., et al., 1961. Laboratory studies of oil recovery by steam injection. *J. Petrol. Technol.* 13 (7), 681–690. <https://doi.org/10.2118/1537-G-PA>.
- Yang, B.Q., Duhamel, J., 2015. Extraction of oil from oil sands using thermoresponsive polymeric surfactants. *ACS Appl. Mater. Interfaces* 7 (10), 5879–5889. <https://doi.org/10.1021/am509231k>.
- Yi, Y.F., Li, S.Y., Ding, F.C., et al., 2009. Change of asphaltene and resin properties after catalytic aquathermolysis. *Petrol. Sci.* 6 (2), 194–200. <https://doi.org/10.1007/s12182-009-0031-y>.
- Zhai, M.K., Du, Q.J., Liu, Y.L., et al., 2022. Potential of a new water-soluble agent for enhancing heavy oil recovery: a pore-scale investigation. *J. Petrol. Sci. Eng.* 208, 109646. <https://doi.org/10.1016/j.petrol.2021.109646>.
- Zhang, B., Liu, Z.Y., Zhang, H., et al., 2022. Molecular selectivity in the water flooding heavy oil process from porous rocks. *RSC Adv.* 12 (38), 24839–24848. <https://doi.org/10.1039/d2ra04721g>.
- Zhao, D.W., Wang, J., Gates, I.D., 2014. Thermal recovery strategies for thin heavy oil reservoirs. *Fuel* 117, 431–441. <https://doi.org/10.1016/j.fuel.2013.09.023>.