

In situ catalytic upgrading of heavy crude oil through low-temperature oxidation

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Abstract The low-temperature catalytic oxidation of heavy crude oil (Xinjiang Oilfield, China) was studied using three types of catalysts including oil-soluble, water-soluble, and dispersed catalysts. According to primary screening, oil-soluble catalysts, copper naphthenate and manganese naphthenate, are more attractive, and were selected to further investigate their catalytic performance in in situ upgrading of heavy oil. The heavy oil compositions and molecular structures were characterized by column chromatography, elemental analysis, and Fourier transform infrared spectrometry before and after reaction. An Arrhenius kinetics model was introduced to calculate the rheological activation energy of heavy oil from the viscosity–temperature characteristics. Results show that the two oil-soluble catalysts can crack part of heavy components into light components, decrease the heteroatom content, and achieve the transition of reaction mode from oxygen addition to bond scission. The calculated rheological activation energy of heavy oil from the fitted Arrhenius model is consistent with physical properties of heavy oil (oil viscosity and contents of heavy fractions). It is found that the temperature, oil composition, and internal molecular structures are the main factors affecting its flow

ability. Oil-soluble catalyst-assisted air injection or air huff-n-puff injection is a promising in situ catalytic upgrading method for improving heavy oil recovery.

Keywords In situ catalytic oxidation · Heavy oil · Upgrading · Low-temperature oxidation · Mechanism

1 Introduction

The resources of heavy oil in the world are more than twice as great as those of conventional light crude oil (Shah et al. 2010). Heavy crude oils, with an API gravity less than 20 (Hascakir et al. 2009), have been found in different regions in the world, such as the Orinoco Belt in Venezuela, Alberta in Canada, some regions of the Gulf of Mexico, and northeastern China (Galarraga et al. 2007; Rana et al. 2007; Hinkle et al. 2008; Chen et al. 2009; Martínez-Palou 2011). However, the compositional complexity and poor flow properties of heavy crude oils bring out many problems and challenges in oil production, transportation, and refining (Sanieri et al. 2004). High contents of unsaturated fractions, mainly resins and asphaltenes in heavy oil are the main factors affecting the viscosity. The recovery of heavy oil faces a challenge because of its high viscosity. Among a variety of enhanced oil-recovery methods, the application of in situ combustion (ISC) process has been regarded as one of the most promising strategies for heavy oil reservoirs. Different from recovery mechanisms of the traditional thermal recovery of hot fluid injection and steam stimulation, the injection of high-pressure air for ISC is the process of injecting air into a reservoir to oxidize a small portion of hydrocarbons in situ for upgrading. The oil viscosity is significantly reduced to initiate heavy oil to flow through porous media. The oil is moved toward the

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production wells by a vigorous drive of flue gases, steam, and hot water. Since it is difficult to reestablish the front, the success of an ISC process mainly depends on the combustion front stability and its rapid propagation. Also oil from the combustion zone is upgraded in situ as the heaviest components burn and the lighter crude oil components evaporate ahead of the combustion front (Zhang et al. 2013). Hence, the quality of the produced oil is improved. Similarly, the aggregation–dissociation phenomenon was detected by Ekulu et al. (2005), showing that high temperatures can degrade the molecular structure of heavy components.

This has stimulated great interest in the application of catalysts to the ISC process in order to accelerate reaction and promote upgrading of reservoir crude oils. Catalysts have the ability to restructure the strongly associating structures as well as rearrange oxygen-containing groups that will effectively reduce the oil viscosity. It is also accepted that the addition of catalysts may promote the breaking of C–S, C–O, and C–N bonds, and hence the chemical properties of heavy oil are changed in favor of liquid flow. Rezaei et al. (2013) and Murillo-Hernández et al. (2009) studied the thermocatalytic influence of nanoparticles and ionic liquids on the oxidation reaction. Lower activation energies were observed for various reactions involved in the combustion process. Kök and Bağcı (2004) investigated catalytic effects of metallic salts on the combustion properties of crude oil by reaction kinetic cell experiments. The reaction had been positively catalyzed and the molar ratio of CO₂/CO of effluent gases increased by additives. Wang et al. (2012) conducted a comparative study of the catalytic effect of tungsten oxide supported on zirconia via different methods to reduce the viscosity of heavy crude oil. With the heavy components converted into light ones and the removal of heteroatoms, the powdered catalyst prepared by the hydrothermal method reduced the viscosity of oil from 5740 to 1020 mPa s, a reduction of 82 %. Upgrading and viscosity reduction of heavy oil by a catalytic ionic liquid and its modified version were investigated by Shaban et al. (2014). With the asphaltenes dissolved by ionic liquids, the oil viscosity reduction increased from 26.8 % to 78.6 % and the sulfur reduction increased to 20 % when the reaction was performed with the modified catalyst at 90 °C. Moore et al. (1999) conducted a combustion tube experiment in the presence of a nickel/alumina catalyst, an 8-point gravity increase was detected for the test Middle East crude of 18° API gravity in addition to a 50 % sulfur removal in the produced oil. Pu et al. (2015) used oxidation tube experiments to study the low-temperature oxidation and characteristics of heavy oil under reaction conditions of 120 °C,

72 h, and 30 MPa. With the addition of the oil-soluble catalyst, cobalt naphthenate to promote the crude oil oxidation, the viscosity of the oxidized oil decreased dramatically. Abuhesa and Hughes (2009) compared the conventional and catalytic ISC process for oil recovery using a low-pressure combustion cell. They found that the presence of a catalyst advanced the combustion reactions and the resultant oil was upgraded by up to 11 points due to several processes such as pyrolysis, distillation, and cracking, which were governed by temperature. Weissman et al. (1996) applied a combustion tube apparatus to down-hole catalytic upgrading of heavy crude oil in the presence and absence of alumina-supported nickel molybdenum, catalytic upgrading was due to hydrogenation and the API of oxidized oil increased from 15.3 to 23.2 with about a 50 % sulfur removal.

Many available published papers state that the presence of catalyst could significantly accelerate the aquathermolysis reaction to further upgrade the quality of heavy oil (Maity et al. 2010; Qin and Xiao 2013; Wu et al. 2013; Shokrlu and Babadagli 2014; Wang et al. 2014). In aquathermolysis, water at high temperatures or in the form of steam plays a crucial role, and the oil viscosity reduces only slightly if water is absent (Wang et al. 2010; Maity et al. 2010). However, the reservoir temperature after steam injection will gradually reduce with an increase in the distance to the wellbore and it is difficult to maintain a relative high temperature, leading to an insufficient energy supply for the catalysis (Liu et al. 2005; Xu et al. 2012b). The production of superheated water or steam is very energy-intensive with a large environmental burden and the necessary process equipment is expensive, resulting in poor economic performance. More to the point, some heavy oils are waterless or oil production areas have extreme water shortages, making it difficult to implement aquathermolysis. Whereas, it is hoped that the oil viscosity can be reduced without adding water and an idea is to apply air injection into heavy oil reservoirs in the presence of catalyst for ISC. Besides, the catalytic oxidation is superior to a single thermal oxidation since it combines the functions of heteroatom reduction, upgrading, splitting of asphaltene and resin, high yields of light components, and accelerated reaction rate.

In this paper, the Xinjiang heavy crude oil was used for the research. We primarily screened different types of catalysts including dispersed, water-soluble, and oil-soluble catalysts by the use of static oxidation tube experiments from the observation of upgrading and viscosity reduction of the target oil. More in-depth analysis was conducted to investigate catalytic oxidation mechanisms at low temperatures.

2 Experimental

2.1 Experimental materials

Heavy crude oil obtained from a reservoir block of the Xinjiang Oilfield (Junggar Basin, China) was used in this study. The reservoir temperature is about 90 °C, the oil viscosity is 3523 mPa s at atmospheric pressure and at 50 °C, and the oil density is 0.938 g/cm³ at atmospheric pressure and at 25 °C.

Three types of catalysts were purchased commercially from the Chengdu Kelong Chemical Reagent Co., Ltd. (Sichuan province, China) and were used as received with the American Chemical Society (ACS) grade. The oil-soluble catalysts are copper naphthenate (Cu(C₁₁H₇O₂)₂) and manganese naphthenate (Mn(C₁₁H₇O₂)₂). The organic ligand is naphthenic acid (C₂₂H₁₄O₄) which serves as the carrier of metal ions to reduce the viscosity of heavy oil and is also crucial to the catalytic performance, and the transition metal ions that serve as catalytic centers are, respectively, Cu²⁺ and Mn²⁺. The dispersed catalyst is copper oxide (CuO), and the water-soluble catalyst is copper dichloride (CuCl₂). The fine quartz used in the experiment was obtained from the Pixian Zhitai Chemical (Sichuan province, China) with 60–80 mesh size. Prior to experiments, the heavy crude oil was separated from the sand to eliminate any catalytic effects arising from other metal salts that might exist in the crude oil. All oil samples were dehydrated to eliminate the effect of dilution and emulsification on viscosity measurement.

2.2 Isothermal oxidation

2.2.1 Experimental setup

Upgrading and viscosity reduction of heavy oil was conducted in a stainless steel reactor. The main body of the reactor was made of a stainless steel tube of 8 mm inside diameter (I.D.), 14 mm outside diameter (O.D.), and 100 cm in length and with an effective volume of 50.3 mL for loading samples. The other equipment used was described in detail in a previous study (Zhao et al. 2012). Figure 1 shows a schematic diagram of the experimental setup for isothermal oxidation of heavy oil.

2.2.2 Experimental procedures

All runs were conducted at 90 °C and at 20 MPa (reservoir conditions) to investigate the catalytic oxidation of heavy oil in porous media. The experimental procedures are as follows: (1) A fixed amount of fine quartz was loaded into the oxidation tube to simulate the porous medium with the

approximate porosity of 38 % and permeability of 2100 mD. (2) The cleaned oil (around 12 mL) mixed with and without different catalysts (catalyst content was 0.5 wt% for each case) was pumped into the oxidation tube at a constant flow rate of 0.5 mL/min to saturate the porous medium. The remaining pore volume was used for compressed air injection, and the outlet of the oxidation tube was shut off. (3) High pressure air was injected into the oxidation tube at a constant rate of 1.0 mL/min until the inlet pressure achieved the required test pressure. Then, the inlet was shut off for performing experiments. At the end of experiments, the oxidation tube was first cooled to room temperature and the oil plus sand mixtures were put into a filter centrifuge for further characterization. All the runs were performed twice to ensure the repeatability and the accuracy of the experimental data.

2.3 Viscosity measurement

The viscosity measurement of the oil sample before and after reaction was conducted with a programmable viscometer (Brookfield DV-III, USA) at 50 °C for screening the most efficient catalysts.

The accuracy of the measurement of oil viscosity is ±1.0 % for a specific spindle running at a specific speed. The viscosity reduction ($\Delta\eta$) of the heavy oil is defined as

$$\Delta\eta = \frac{\eta_0 - \eta}{\eta_0} \times 100\%,$$

where $\Delta\eta$ is the percentage of reduction in the oil viscosity; η_0 and η are the oil viscosity before and after reaction, respectively.

The target oil samples were heated to 100 °C and held constant for a few minutes. Then these oils were cooled down from 100 to 40 °C at a rate of 0.5 °C/min, and the viscosity at different temperatures was measured during the cooling process.

2.4 Oil sample separation and characterization

To obtain enough material for further analysis, four group compositions including saturates, aromatics, resins, and asphaltenes were separated from oil samples by a chromatography column according to the industrial standard of China Petroleum SY/T 5119. The elemental composition of oils (C, H, O, N, and S) was measured by an elemental analyzer (Elementar Vario EL-III, Germany). The structural changes of heavy oil before and after reaction were characterized by Fourier transform infrared spectroscopy (FT-IR WQF-520, China).

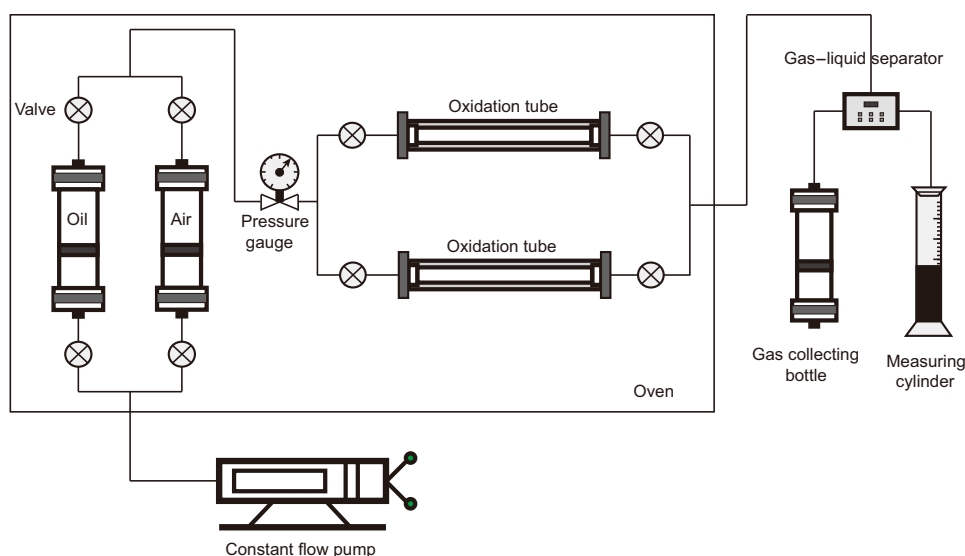


Fig. 1 Schematic diagram of the setup for isothermal oxidation of heavy oil

3 Results and discussion

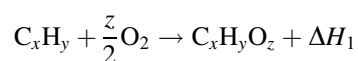
3.1 Analyses of viscosity reduction mechanisms and oxidation models

It is widely accepted that the high content of resins and asphaltenes in heavy oil is responsible for high viscosity (Chao et al. 2012). The viscosity enhancing effect of the resins on heavy oil is due to a large number of heteroatoms contained. This promotes the formation of complex structures between family molecules, with little relationship with the size of the resin itself. In the asphaltene case, in addition to its own high viscosity, its viscosity enhancing effect is more reflected in the impact of micelles formed by interaction on the viscosity (Li et al. 2010). When the resins and aromatics in heavy oil are not enough to surround the asphaltenes to form micelles, the asphaltene molecules are likely to further associate with each other to form large clumps and coagulations, which greatly increase the viscosity of heavy oil. The approaches of viscosity reduction upon treatment of heavy crude oil with catalysts are mainly from two aspects. Intermolecular forces with weak bond energies expressed such as hydrogen bond, coordination bond, and van der Waals force are easy fractured, resulting in that the tight association structure in heavy oil becomes loose. The small molecules wrapped inside the heavy oil molecular aggregates are released and the viscosity undergoes reversible reduction. On the other hand, part of the chemical bonds with weak bond energies (C–C, C–O, and C–S bonds) are ruptured, leading to scission reactions for alkyl side chains and generating chain bridges, heterocyclic rings, etc. With heavy substances converting to light components, the molecular aggregation is weakened along with a decrease

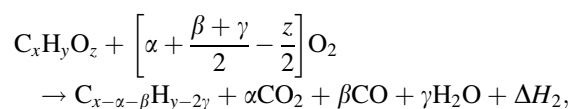
in the average relative molecular weight, and the viscosity reduces irreversibly. It is acknowledged that condensed aromatic rings form the main structure of resin and asphaltene. Rich fatty structural units connected to the aromatic rings, complex branched structures, and a high degree of aromatization make the molecular structure exhibit strong polarity and make it easy to be attacked by oxygen atoms, which contribute to a fast oxidation reaction rate and large reactivity for resin and asphaltene at low temperatures (Castro and Vazquez 2009; Chen et al. 2013b).

In general, there will be a series of reactions between crude oil and oxygen once they are in contact. Oxygen atoms are first bound into the carbon chains and the hydrocarbon compounds are converted into ketones, aldehydes, alcohols, and other partially oxidized materials (Kapadia et al. 2013). After that, the chain scission reaction occurs. In this process, hydrocarbon products keep reacting with oxygen, whilst chains with functional groups are split into carbon dioxide, carbon monoxide, water, and shorter chain hydrocarbon compounds. A two-step reaction mode can be used to describe the oxygen addition reaction and decarboxylation process described elsewhere (Zhao et al. 2012).

Step 1 (oxygen addition reaction):



Step 2 (decarboxylation reaction):



where ΔH is the reaction enthalpy and x , y , z , α , β , and γ are the stoichiometric coefficients of the chemical reaction. The oxygen addition reactions can cause a dramatic increase in the oil viscosity with the formation of heavier, less desirable oil fractions. On the contrary, the decarboxylation reactions can reduce the viscosity of crude oil with the generation of shorter chain hydrocarbon compounds. It seems that there is a competition for the predominant role between the two types of reactions at low temperatures (Barzin et al. 2010).

3.2 Viscosity reduction with different types of catalysts

The viscosity of oil samples before and after oxidation reaction with different types of catalysts are shown in Fig. 2. This shows that the viscosities of oil samples after reaction increased from the original value 3523 mPa s, respectively, to 4731 and 4196 mPa s for the dispersed and water-soluble catalysts, while to 1238 and 1705 mPa s for the oil-soluble catalysts ($\text{Cu}(\text{C}_{11}\text{H}_7\text{O}_2)_2$) and ($\text{Mn}(\text{C}_{11}\text{H}_7\text{O}_2)_2$). The dispersed and water-soluble catalysts failed to reduce the viscosity of heavy oil, with thickening ratios of 34.3 % and 19.1 %, respectively, while the oil-soluble catalysts exhibited excellent capacity to reduce the oil viscosity. The compared results indicate that the oil-soluble catalysts are the most active catalysts for catalytic oxidation of heavy crude oils, aiming to reduce the oil viscosity.

The viscosity variation of heavy oil catalyzed by different types of catalysts can be explained as follows. According to low-temperature oxidation models, it is believed that the dispersed and water-soluble catalysts, CuO or CuCl_2 can accelerate the chemical combination of oxygen with liquid hydrocarbons to form hydroperoxides,

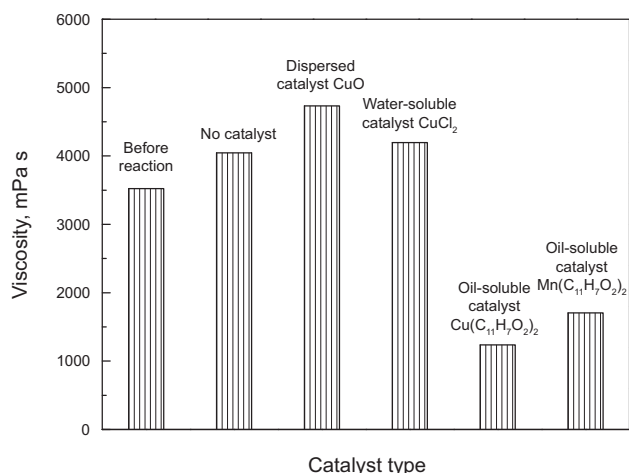


Fig. 2 Viscosity variations of oil samples before and after catalytic oxidation over different catalysts

which tend to further react and polymerize with each other (Niu et al. 2011), and the oxygen addition reaction plays a predominant role. As well, the molecular size of hydrocarbons increases and the structure becomes more complicated. Under the action of molecular forces, the macromolecules with oxygen-containing functional groups aggregate and associate mutually to form supermolecular structures with various levels, leading to an increase in viscosity. As to the oil samples catalyzed by oil-soluble catalysts, experimental results indicate that the reaction mode may be changed easily from oxygen addition switching to bond scission. Homogeneous catalysis may be another reason for the superiority of the oil-soluble catalysts $\text{Cu}(\text{C}_{11}\text{H}_7\text{O}_2)_2$ and $\text{Mn}(\text{C}_{11}\text{H}_7\text{O}_2)_2$. To better understand the role of oil-soluble catalysts in reducing the viscosity of heavy oil, a blank experiment was carried out under the same conditions without a catalyst. Figure 2 shows that the oil viscosity increased from 3523 mPa s (original value) to 4047 mPa s (after oxidation), which further proves that the introduction of oil-soluble catalysts $\text{Cu}(\text{C}_{11}\text{H}_7\text{O}_2)_2$ and $\text{Mn}(\text{C}_{11}\text{H}_7\text{O}_2)_2$ can significantly promote the viscosity reduction of heavy oil.

The viscosity of these oil samples was measured at 50 °C. Since the wax contents in crude oil, and oil catalyzed by oil-soluble catalysts $\text{Cu}(\text{C}_{11}\text{H}_7\text{O}_2)_2$ and $\text{Mn}(\text{C}_{11}\text{H}_7\text{O}_2)_2$ were 2.11 %, and 1.46 % and 1.42 %, respectively, and the melting point of microcrystalline wax is usually around 70 °C, viscosity measurement at 80 °C is meaningful for heavy oil. It will help us to focus on studying the effects of asphaltene and resin, which are usually regarded as the primary cause of high viscosity for heavy oil (Ghanavati et al. 2013; Wang et al. 2014). In order to avoid the influence of wax during viscosity measurement, the viscosity of oil samples catalyzed by oil-soluble catalysts was subsequently measured at 80 °C. The viscosity reduction of oil samples is summarized in Fig. 3. After catalytic oxidation at low temperatures, the viscosity of the oil sample, measured at 50 °C, reduced by 64.9 % and 48.2 %, respectively, for the oil-soluble catalysts $\text{Cu}(\text{C}_{11}\text{H}_7\text{O}_2)_2$ and $\text{Mn}(\text{C}_{11}\text{H}_7\text{O}_2)_2$; while the oil viscosity reduced by 51.6 % and 40.4 % for the two catalysts when the viscosity was measured at 80 °C. The viscosity of the original crude oil was 3523 and 441.36 mPa s at 50 and 80 °C.

However, the viscosity reduction of oil samples measured at 80 °C was lower than that tested at 50 °C, which also confirms the effect of microcrystalline wax on the heavy oil viscosity. The thickening ratio at 80 °C was 4.9 % in the controlled experiment. The oil-soluble catalysts could drastically reduce the viscosity of heavy oil, and the oil-soluble catalyst $\text{Cu}(\text{C}_{11}\text{H}_7\text{O}_2)_2$ was more effective than the oil-soluble catalyst $\text{Mn}(\text{C}_{11}\text{H}_7\text{O}_2)_2$. In the subsequent study, we selected the two oil-soluble catalysts to

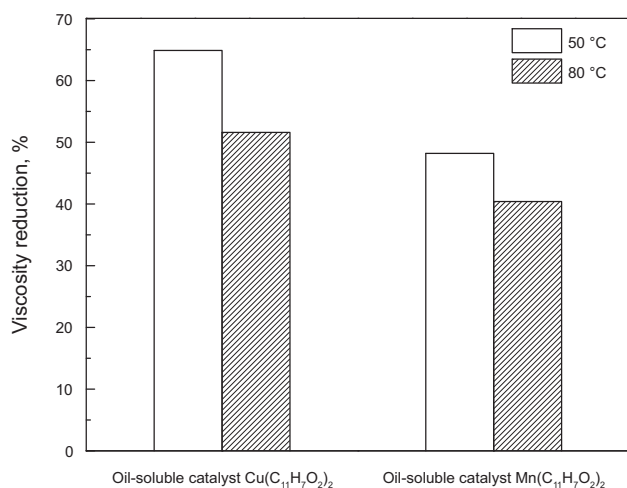


Fig. 3 Viscosity reduction of heavy oil after catalytic oxidation

further investigate the oxidation performance of heavy oil over these oil-soluble catalysts.

3.3 Composition variation of heavy oil before and after oxidation

Table 1 summarizes the group compositions of heavy oil before and after catalytic oxidation with oil-soluble catalysts Cu(C₁₁H₇O₂)₂ and Mn(C₁₁H₇O₂)₂, which were determined based on the method for determining the contents of wax, resins, and asphaltenes in crude oil (SY/T 7550-2004). It should be noted that the content of each unsaturate is a relative weight content without saturates. The composition changes of oil samples show an increase in the contents of saturates and aromatics and a loss in resins and asphaltenes after reaction, verifying that the oil-soluble catalysts have the ability to crack part of heavy components (asphaltenes and resins) into light components (saturates and aromatics) (Qin and Xiao 2013). As we know, the resins and asphaltenes consist primarily of condensed aromatic rings, naphthenic rings, alkyl side chains, and heteroatoms. The macroscopic decrease in the content of heavy components implies the probable pyrolysis of C–R (R=S, N, and O) bonds in terms of microscopic molecular structure. The C–S bond is believed to be one of the weakest bonds in heavy oil molecules. It is also found that catalysts can lead to the splitting of a few C–O and C–

N bonds owing to the emergence of a variety of oxygen-containing and nitrogen-containing compounds in the reaction products (Chen et al. 2010, 2011b). The participation of transition metal ions can attack heteroatoms of macromolecules of heavy components to perform the catalytic process, such as pyrolysis, decarboxylation, hydrodesulfurization, depolymerization, isomerization, and ring opening. The C–R (R=S, N, and O) bonds will be weakened and break easily at high temperatures, resulting the heavy components to be depolymerized to form fragments with different sizes. Another reason for composition changes in this study is the generation and accumulation of a large number of free radicals with high reactivity during oxidation according to Sarma et al. (2002). The exothermic reaction pathways are opened, wherein highly reactive free radicals are generated. The catalysis is believed to be related to these highly reactive free radicals to improve the quality of heavy crude oil.

In terms of low-temperature oxidation models, oxygen is firstly in combination with liquid hydrocarbons to form oxygen-containing functional groups, mainly ketones, aldehydes, and alcohols (Chen et al. 2013a). Generally, these medium products are unstable and are vulnerable to bond scission reactions. Hydrocarbon products keep reacting with oxygen, and thus the chains with oxygen-containing functional groups are further broken down to carbon monoxide, carbon dioxide, water, and shorter chain hydrocarbon compounds. Zhang et al. (2015) investigated the characteristics of low-temperature oxidation (LTO) of heavy oils through laboratory experiments and found that the heavy components served as the main reactant in the LTO process. During the oxidation, the carbon chains of heavy components were broken, producing some light components and leading to a relative decrease in the total content of heavy components. Similar phenomena have also been found in other published studies (Yu et al. 2008; Tang et al. 2011; Li et al. 2013b). Because the branched chains are more easily broken than linear chains, and chain scission happens more easily than dehydrogenation and oxygenation in the same carbon number alkane, oxygen addition and chain scission will play a predominant role in this stage despite the carbon chains undergoing a polycondensation process at the same time. Meanwhile, with the effect of oil-soluble catalysts, the transition of the predominant reaction mode from oxygen addition to bond

Table 1 Variation of group compositions of heavy oil

Oil sample	Catalyst	Content, %		
		Saturates + aromatics	Resins	Asphaltenes
Before reaction	–	45.07	46.62	8.31
After reaction	Oil-soluble catalyst Mn(C ₁₁ H ₇ O ₂) ₂	51.49	44.77	3.74
After reaction	Oil-soluble catalyst Cu(C ₁₁ H ₇ O ₂) ₂	54.12	43.73	2.15

scission can be easily achieved, which is verified by the viscosity reduction of 65 % and 52 % for oil-soluble catalysts $\text{Cu}(\text{C}_{11}\text{H}_7\text{O}_2)_2$ and $\text{Mn}(\text{C}_{11}\text{H}_7\text{O}_2)_2$, respectively, at 50 °C. The catalytic oxidation of crude oil is from the attack of oxygen atoms. The long alkyl side chains and naphthene groups located on the polycyclic aromatics in resin and asphaltene are likely to cleave and open the rings, leading to a decrease in resins and asphaltenes as well as an increase in saturates and aromatics (Li et al. 2013a).

Table 1 shows that the content of heavy components (resins and asphaltenes) decreased by 6.4 % and 9.0 %, respectively, after oxidation of heavy oil with catalysts $\text{Mn}(\text{C}_{11}\text{H}_7\text{O}_2)_2$ and $\text{Cu}(\text{C}_{11}\text{H}_7\text{O}_2)_2$. Similar to viscosity reduction, the experimental results demonstrate that the catalyst $\text{Cu}(\text{C}_{11}\text{H}_7\text{O}_2)_2$ shows high activity in the aspect of upgrading heavy components. Table 1 also indicates that the resin content, respectively, decreased by 2.89 % and 1.85 % after oxidation over catalysts $\text{Cu}(\text{C}_{11}\text{H}_7\text{O}_2)_2$, and $\text{Mn}(\text{C}_{11}\text{H}_7\text{O}_2)_2$, while asphaltene content decreased by 6.16 % and 4.57 %, implying that the two catalytic ions mainly react with asphaltene. The different catalytic performances of additives are related to the molecular structure differences between resin and asphaltene. This is due to the fact that asphaltenes have longer alkyl branch sides, more layer structures, and higher average molecular weight than the resins. From another perspective, it is known that some of the resins can crack into saturate or aromatic fractions, and asphaltenes can split into resin during thermolysis (Wang et al. 2009). Intuitively, the cracking of original resins can decrease their content only to a limited degree, but the new resins generated by asphaltene splitting can compensate for the cracking loss of original resins. Hence, the overall content of resins only changes slightly.

3.4 Elemental analysis of heavy oil before and after reaction

Elemental analysis results of heavy oil before and after oxidation are summarized in Table 2. It can be seen that the contents of carbon and heteroatoms (S, O, and N) decreased after low-temperature catalytic oxidation, while for the hydrogen content and the atomic ratio of H to C, $N_{\text{H}}/N_{\text{C}}$, of oil samples a reverse tendency was observed. Among these changes, the removal of heteroatoms is related to the cleavage of C–R (R=S, O, N) bonds. It is not

surprising that the change of content of S is more evident than those of O and N after oxidation. It can be explained as the bond energy of C–S is relatively low (Hyne and Greidanus 1982). Meanwhile, during the upgrading process, the combination of a metallic ion in the catalyst with a S atom can weaken C–S bonds and cause the breakage of heavy oil molecules. By contrast, since the C–N bond is the most stable bond among other bonds of molecules in the oil, most of nitrogen remains in the heavy component molecules after reaction, resulting in a lesser decrease in its content compared with other heteroatoms. Also, the atomic ratio of H to C of reacted oil over the oil-soluble catalysts increased, which is due to the cracking of weak C–C bonds in heavy hydrocarbons.

API gravities of original heavy crude oil and oil samples catalyzed by oil-soluble catalysts $\text{Mn}(\text{C}_{11}\text{H}_7\text{O}_2)_2$ and $\text{Cu}(\text{C}_{11}\text{H}_7\text{O}_2)_2$, were 19.2, 23.3, and 24.7, respectively. Because even a small fraction of bond splitting can lead to a significant improvement of the flow properties of heavy oil, the cleavage of some C–R (R=S, N, and O) bonds favors reducing crude oil viscosity eventually with the quality slightly upgraded after oxidation. In addition, when many heavy oil molecules split into fragments, the total number of rings is reduced and some of saturated fragments will release light components, leading to an increase in the content of saturates and aromatics. In general, the changes of heavy oil compositions and molecular structures are responsible for viscosity reduction and quality improvement. The changes of elemental contents after catalytic oxidation over the catalyst $\text{Cu}(\text{C}_{11}\text{H}_7\text{O}_2)_2$ are more obvious than that over the catalyst $\text{Mn}(\text{C}_{11}\text{H}_7\text{O}_2)_2$, which means that the catalyst $\text{Cu}(\text{C}_{11}\text{H}_7\text{O}_2)_2$ is superior to the catalyst $\text{Mn}(\text{C}_{11}\text{H}_7\text{O}_2)_2$ for splitting heavy oil molecules.

A comparison of elemental composition between the Xinjiang heavy oil and other heavy oils in previous studies has also been made in terms of catalytic reaction (Wang et al. 2012; Xu et al. 2012a; Qin and Xiao 2013). It is easy to find from Table 3 that the changing trends of elements are consistent with the Xinjiang heavy oil catalyzed by oil-soluble catalysts. In these experiments, the heteroatoms were removed and the values of $N_{\text{H}}/N_{\text{C}}$ increased after catalytic reaction, which is a positive sign for heavy oil upgrading. For example, Qin and Xiao (2013) investigated the effects of the oil-soluble catalyst (Fe^{2+}) on elemental

Table 2 Elemental analysis of heavy crude oil

Oil sample	Catalyst	Content, %					$N_{\text{H}}/N_{\text{C}}$
		C	H	O	N	S	
Before reaction	–	81.69	12.95	1.76	0.93	2.64	1.90
After reaction	Oil-soluble catalysts $\text{Mn}(\text{C}_{11}\text{H}_7\text{O}_2)_2$	80.21	15.23	1.31	0.78	1.59	2.28
After reaction	Oil-soluble catalysts $\text{Cu}(\text{C}_{11}\text{H}_7\text{O}_2)_2$	79.94	15.81	1.19	0.72	1.36	2.37

Table 3 Comparison of elemental composition of heavy oil from the literature

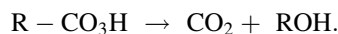
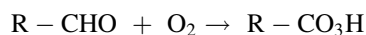
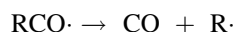
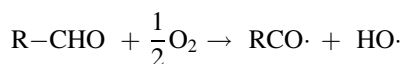
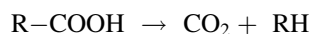
	Catalyst	Before reaction						After catalytic reaction					
		C, %	H, %	O, %	N, %	S, %	N_H/N_C	C, %	H, %	O, %	N, %	S, %	N_H/N_C
Wang et al. (2012)	20-W/Zr-HD-650	86.63	11.47	–	1.00	0.90	1.59	86.06	12.25	–	0.99	0.70	1.71
Qin and Xiao (2013)	Fe ²⁺ -catalyst	81.20	13.70	1.26	0.95	0.28	2.02	79.50	16.70	0.42	0.91	0.05	2.52
Xu et al. (2012a)	Cu ²⁺ -catalyst	80.23	11.77	2.76	1.96	3.28	1.76	81.24	12.64	2.16	1.75	2.21	1.87

compositions of heavy oil during steam huff and puff. The results showed that the Fe²⁺-catalyst could effectively decrease the amounts of heteroatoms (S, O, and N) after the upgrading process. Meanwhile, the atomic ratio of H to C, N_H/N_C increased and the quality of the heavy oil was also improved after treatment. The comparison indicates that the oil-soluble catalyst should be a favorable catalyst for viscosity reduction and upgrading of heavy oil.

3.5 FT-IR spectra of heavy oil before and after reaction

Figure 4 shows the FT-IR spectra of heavy oil before and after reaction. An absorption peak at 3344 cm⁻¹ was observed to become stronger after low-temperature oxidation without a catalyst, indicating the occurrence of alcohol addition reactions. As well, the bands between 1705 and

1597 cm⁻¹ were enhanced, which could be attributed to the formation of new carbonyl groups (C=O), such as carboxylic acids, ketones, aldehydes, and others favored by the degradation of hydroperoxides (Chao et al. 2012). It is believed that there could be numerous reactions between crude oil and oxygen once they are in contact. Under the attack of oxygen atoms, carbon–hydrogen bonds in hydrocarbon components split to generate oxygen-containing groups. Accordingly, comparative results of Fig. 4a, b indicate that the oxygen addition reaction plays a predominant role during the low-temperature oxidation without a catalyst. By comparing Fig. 4b, c the absorption peak at 3344 cm⁻¹ became weaker, indicating that some of alcohol functional groups were removed; the observed bands in 1705–1597 cm⁻¹ were weakened, which could be attributed to breakage of C=O bonds and the occurrence of hydrogenation reaction. Due to the catalytic effect of the oil-soluble catalyst, the contents of oxygen-containing groups decreased. Bond scission reactions are responsible for the further reaction of oil oxides and dominates the reaction modes. The reaction schemes can be shown through to Chen et al. (2013a), as shown below:



It is concluded that the oil-soluble catalyst has the capability to cause the transition of the reaction mode from oxygen addition to bond scission. In comparison with Fig. 4a, absorption peaks in Fig. 4c at 1023 and 1162 cm⁻¹ were weakened, and the absorption peak at 1267 cm⁻¹ has nearly disappeared, indicating the breakage of C–N, C–O, and C–S bonds; the absorption peak at 796 cm⁻¹ was also weakened, showing the removal of the existing alkyl side chain; the absorption peak at 868 cm⁻¹ became weaker, implying the occurrence of ring-opening reactions (Castro and Vazquez 2009). As well, the absorption peak at 1374 cm⁻¹ was enhanced in Fig. 4b while being reduced in Fig. 4c, showing the aggregation of condensed aromatic

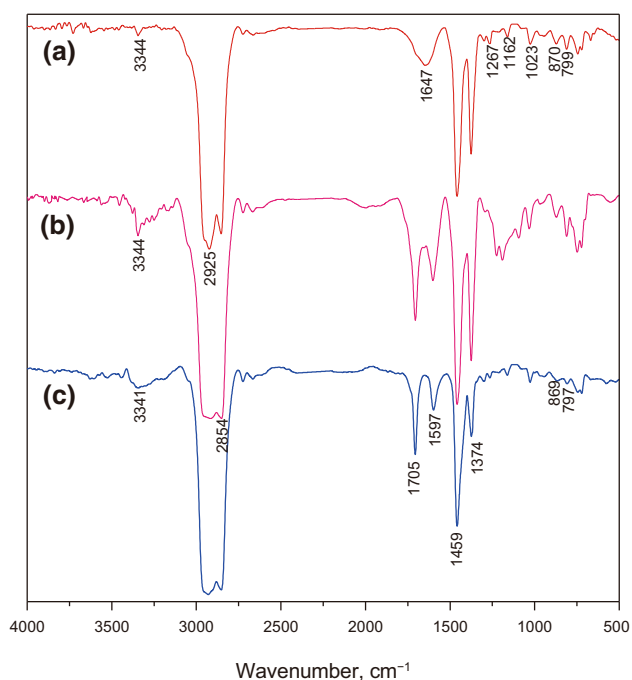


Fig. 4 FT-IR spectra of heavy oil. **a** Before reaction. **b** After reaction without a catalyst. **c** After reaction with the oil-soluble catalyst Cu(C₁₁H₇O₂)₂

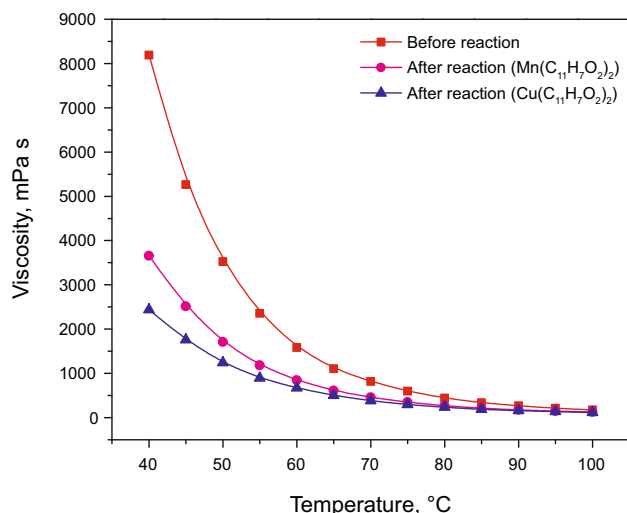


Fig. 5 Viscosity–temperature curves for oil samples

rings during the oxidation without a catalyst and the addition of the oil-soluble catalyst could inhibit the polymerization. All these changes also indicate that some of heteroatoms were removed and the tight macromolecular rings were reduced to fragments of different sizes, which is consistent with the result of the elemental analysis.

3.6 Analysis of viscosity–temperature characteristics

3.6.1 Temperature sensitivity

The complexity of the microstructure of heavy oil results in viscosity–temperature characteristics different from its macroperformance. The viscosities of heavy oil before and after catalytic reaction were measured and analyzed from the microscopic point of view. Figure 5 shows that the viscosity of heavy oil exhibited strong temperature sensitivity. The viscosity of oil samples changed smoothly when the temperature was higher than 60 °C during the cooling process, while rapidly increasing when the temperature was below 60 °C, and the lower the temperature, the more dramatic the change in viscosity. This is due to heavy oil being a multiphase liquid mixture. The relative size, distribution, and content of macromolecular solid particles (e.g., asphaltenes) in the liquid, as well as the momentum exchange between different components, agglomerating by association and arrangement mode, significantly affect the viscosity of heavy oil. Most crude oil is a relatively stable colloidal dispersed system, in which the asphaltene is the core of the dispersed phase (Ye et al. 2010). The compositions gradually change from the centers of micelles to the dispersion medium. Connection or disassembly of these micelles loosens the internal structure and lowers the

cohesive force in crude oil, which is the essence of viscosity–temperature characteristics.

Regression analysis was applied to the viscosity–temperature relationship of heavy oil before and after catalytic oxidation, and the regression equation conforms to the Arrhenius equation perfectly. The Arrhenius equation is of the form (Zhu et al. 2011, 2012):

$$\eta = 1000 A \exp(E/RT),$$

where η is the oil viscosity, mPa s; E is the activation energy, kJ mol^{-1} ; R is the universal gas constant; T is the measured temperature, K; A is a constant. Taking the logarithm of both sides and the final form of the kinetic model used for analysis is as follows:

$$\log \eta = \log 1000 + \log A + E/(2.303RT).$$

The viscosity–temperature curve is converted into a $\log \eta - 1/T$ curve and the results are shown in Fig. 6. The curves are not straight lines in the strict sense. With an increase in $1/T$, $\log \eta$ gradually deviates upward. This indicates that not only the van der Waals force plays a role between micelles, but also the molecular structure has changed inside the crude oil, both of which lead to the viscosity increasing rapidly during the cooling process (Huang et al. 2014). There is no apparent inflection point in the curve and the curve is curved upward smoothly, indicating that the internal molecular structure of heavy oil gradually changes during the cooling process and no obvious phase transformation point occurs. The $1/T$ is roughly divided into three intervals according to the variation tendencies of the curve. When $\log \eta$ is plotted vs. $1/T$ for each interval, a straight line is obtained, and the values of E can be calculated from the slope of the linear

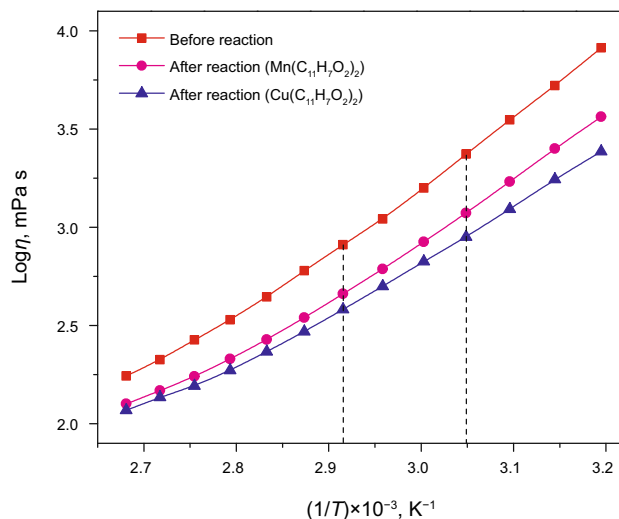


Fig. 6 Relationship curves between $\log \eta$ and $1/T$ during the cooling process

fit. Kinetic parameters of all oil samples are summarized in Table 4 in detail.

The correlation coefficient of linear fit in each temperature interval is more than 0.9889, indicating that the curves conform to the Arrhenius equation. *E* is the value of activation energy which refers to the energy barrier that must be overcome to form a cavity near the particle and large enough for particle to move before the fluid begins to flow. It is a measure of the friction force between particles inside the fluid, which depends on the polarity of particles, molecular mass, and molecular configurations. In the high temperature interval (from 70 to 100 °C), the activation energies of oil samples decrease with the following sequence, i.e., oil before reaction, oil after reaction with the catalyst Mn(C₁₁H₇O₂)₂, and oil after reaction with the catalyst Cu(C₁₁H₇O₂)₂. These results correspond to the variation of four group compositions of heavy oil in Table 1. In the other two temperature interval cases, this consistency is also detected. The reason may be that the unreacted crude oil contains more heavy components (resins and asphaltenes) and less light components (saturates and aromatics) than the catalytically oxidized heavy oil. Actually, a higher content of heavy components can provide larger molecules, and the interaction force is stronger between various molecules, hence, higher activation energy is needed for molecule flow (Chen et al. 2011a). It will lead to the macrophenomena of high viscosity for crude oil. Besides, intermolecular hydrogen bonds can also increase the viscosity of crude oil. The rheological activation energy of the oil sample after reaction with the catalyst Cu(C₁₁H₇O₂)₂ is the lowest, which further demonstrates that the catalyst Cu(C₁₁H₇O₂)₂ is more favorable for heavy oil viscosity reduction compared to the catalyst Mn(C₁₁H₇O₂)₂.

It can be seen from Table 4 that the activation energies are different in various temperature intervals for the same oil sample, and the activation energy at low temperatures is higher than that at high temperatures. There are several reasons contributing to the increase in the activation energy at low temperatures. (1) During the cooling process, the degree of the thermal motion of particles is weakened and the solubility of resin in heavy oil reduces, resulting in resin molecules continuously precipitating from crude oil. These can absorb and aggregate on the surfaces of asphaltene particles to form a solvent layer of varying thickness (Ye et al. 2010). This adsorption effect becomes significant as well as an increase in the solvent layer at lower temperatures. The aggregated asphaltene adsorbs the solvent layer during the cooling process, resulting in increases in the micelle volume and the interaction force. (2) At low temperatures, with an increase in the volume of resin–asphaltene aggregations, the distance between micelles is reduced. Adjacent micelles may be connected

Table 4 Kinetic parameters of oil samples before and after reaction

Temperature intervals, °C	Before reaction			After reaction (catalyst Mn(C ₁₁ H ₇ O ₂) ₂)			After reaction (catalyst Cu(C ₁₁ H ₇ O ₂) ₂)		
	Regression equation	R ^{2a}	E, kJ/mol	Regression equation	R ²	E, kJ/mol	Regression equation	R ²	E, kJ/mol
70–100	log η = -5.4 + 2868.7/T	0.9960	54.93	log η = -4.3 + 2393.6/T	0.9916	45.83	log η = -3.8 + 2184.8/T	0.9889	41.83
55–70	log η = -7.2 + 3467.2/T	0.9966	66.38	log η = -6.3 + 3085.2/T	0.9993	59.07	log η = -5.5 + 2772.2/T	0.9994	53.08
40–55	log η = -7.8 + 3690.9/T	0.9997	70.67	log η = -7.2 + 3370.9/T	0.9996	64.54	log η = -6.1 + 2994.3/T	0.9998	57.33

^a R² stands for the correlation coefficient of linear fit line

with each other through the action of hydrogen bonds and coordinative bonds to form a spatial network structure and to wrap a lot of liquid oil in it (Zhu et al. 2011, 2012). (3) A small amount of paraffin contained in crude oil crystallizes and precipitates at low temperatures, and interacts with resin and asphaltene in the precipitation process, giving the heavy oil significant structural strength at low temperatures. All of these lead to a rapid increase in viscosity at low temperatures, and this is why the $\log\eta$ versus $1/T$ curve has greater deviation upward at low temperatures. Hence, it is crucial for production of heavy crude oil to maintain the reservoir at relatively high temperatures if possible.

On the basis of analysis of activation energy for various oil samples, it is found that the surrounding temperature, oil composition, and internal molecular structure are the main factors affecting the flow capability of heavy crude oil under reservoir conditions. As is known, in situ combustion is a thermally enhanced recovery method that promotes combustion reactions between a small portion of hydrocarbons in place and the injected air to generate heat in the reservoir. Viscosity is significantly reduced due to heat release in exothermic reactions, resulting in some asphaltene molecules splitting to small molecules. Hence, the flow properties of heavy oil are improved (Xu et al. 2012b). Moreover, the generated heat provides the driving force for viscous oil to flow easily to achieve high displacement efficiency. Besides, compared with traditional steam-based recovery processes, heat loss is avoided as energy generation is performed within the oil-bearing zone. On the other hand, the elemental content and molecular structure of oil samples have been changed after low-temperature catalytic oxidation with oil-soluble catalysts. Part of the heavy components, mainly resin and asphaltene fractions are converted into light components, such as saturated and aromatic fractions, leading to in situ upgrading and viscosity reduction of heavy crude oil. We believe that catalytic assisted air injection (or huff and puff) should be a favorable thermally enhanced oil recovery method for heavy crude oil.

4 Conclusions

- (1) Oil-soluble catalysts are found to be the most effective catalysts for reducing the viscosity of heavy crude oil and upgrading the heavy crude oil when implementing low-temperature catalytic oxidation. Copper naphthenate $\text{Cu}(\text{C}_{11}\text{H}_7\text{O}_2)_2$ shows more favorable catalytic effects than manganese naphthenate $\text{Mn}(\text{C}_{11}\text{H}_7\text{O}_2)_2$.
- (2) The combined analyses of group composition, elemental content, and FT-IR spectra indicate that part of heavy components (asphaltenes and resins) may

split into light components (saturates and aromatics) during low-temperature oxidation with oil-soluble catalysts and then heavy crude oil is upgraded. The catalyst plays an important role in promoting the oxidation-cracking reaction and has the ability to switch the reaction mode from oxygen addition to bond scission.

- (3) The viscosity of heavy crude oil is intensively sensitive to temperature, and the oil viscosity increases rapidly with a decrease in temperature when the temperature is lower than 60 °C. A regression analysis is applied to study the viscosity–temperature relationship of oil samples, exhibiting the goodness fit of an Arrhenius model. The calculated activation energies correspond to the physical characteristics of viscosity and heavy component content.
- (4) The surrounding temperature, oil composition, and internal molecular structure are the main factors affecting heavy crude oil flow ability. Implementing oil-soluble catalyst assisted air injection or air huff-and-puff injection should be a favorable strategy to improve heavy crude oil recovery.

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