Full Length Article

A mechanism study on the viscosity evolution of heavy oil upon peroxide oxidation and pyrolysis

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ABSTRACT

In the present work, we investigate the viscosity evolution of heavy oil by peroxide oxidation and successive thermal pyrolysis. Our results show that, the oxidation majorly occurs in the aromatic hydrocarbon (AH), which may debranch the side chains of aromatic derivatives forming isolated long-chain carboxylic acids, or introduce carboxyl to the tail of the branch chains in aromatic structures. The elevated interactions between adjacent debranched side chains in AH as well as condensation of the AH fragments will occur, which will transfer the AH components to resins and result in a quasi-linear correlation between the viscosity and total acid number (TAN) of heavy oil. Upon pyrolysis, resins in original heavy oil will be fragmented accompanied with decarboxylation; while the prior oxidation to heavy oil, although increases the viscosity, will benefit the fragmentation and decarboxylation, leading to approximate viscosity reduction behavior. Our work reveals that the oxygen content should be an important factor that contributes to the high viscosity of heavy oil, which could render reliable reference for developing new strategies to efficiently recover heavy oil reservoirs.

1. Introduction

Heavy oil, existing worldwide (Canada, Mexico, Venezuela, and China etc) [1], has become an increasingly important unconventional energy resource in recent decades [2]. However, its compositional complexity as well as high viscosity have put significant technical challenges to exploitation and utilization [3–5]. Many upgrading approaches, including chemical exploitation [6], physical recovery [7] and biological upgradation [8], have been developed to reduce the viscosity of heavy oil for efficient recovery, which depend strongly on the fundamental origin of the high viscosity of heavy oil. It has been well cognized that the condensation of fused polycyclic arenes as well as the twine of long-chain aliphatics and naphthenics are the dominative factors that govern the grade of viscosity [9–11]. Beyond the major C and H elements, a certain content of N and S heteroatoms, originated from kerogen deposit [12,13], are mainly presented in the heterocyclic compounds, which would bring excessive viscosity increment [14,15]. In fact, hydrogenation of the unsaturated structures and elimination of the heteroatoms have been reported to be capable of weakening the dense packing of polycyclic compounds and consequently decreasing the viscosity of heavy oil [16,17].

In contrast, most heavy oil contains a noneligible content of O due to the oxidation, biodegradation and water washing during migration [18], especially for secondary heavy oil, resulting in elevated viscosity

[19,20]. Fassihi et al. suggested that artificial oxidation by ambient air of crude oil will increase the content of resins or asphaltenes or even lead to coke generation at low temperature [21]; when using compressed air to undergo the oxidation, as reported by Carbognani et al., the resins and asphaltene components could even be precipitated [22]. Apparently, the oxidation process should plant large amounts of O-containing groups in the components of heavy oil. Specifically, unlike N and S heteroatoms, O species generally occur as $-COOH$, $-C=O$, $-OH$ and $-C-O-C-$ groups in aliphatic and naphthenic components [23]. Particularly, carboxylic acids are the dominative O-containing compounds in resins [24]. These groups would exert considerable polarity to increase the Van der Waals interaction in the aliphatics and naphthenics, leading to higher degree of crosslinking. Furthermore, the acidic components in crude oils would result in serious corrosion to industrial units in refineries [25]. Thereby, treatment with alkali to neutralize acids has also been proven to be an efficient method for heavy oil recovery [26,27]. On the other aspect, under a high-temperature heavy oil upgradation such as catalytic aquathermolysis or thermal pyrolysis, CO_2 generation can be always observed, which could be ascribed to the decarboxylation of carboxylic components in heavy oil [28,29]. These efforts clearly indicate that the O-containing components especially the carboxylic acids should also play an essential role for the high viscosity of heavy oil. However, an explicit description to the relationship between O content and the viscosity of heavy oil is

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still absent.

In the present work, we carried out a set of oxidation experiments (100 °C, 12 h) and thermal pyrolysis (240 °C/2 MPa, 12 h) of Tahe heavy oil to investigate the viscosity evolution. The O content, viscosity, TAN (total acid number) and four components of the original and oxidized heavy oil samples before and after thermal pyrolysis were measured. FT-IR and GC–MS characterization of the extracted acidic components were conducted to ascertain the structure of the carboxylic acids. The mechanism of the heavy oil viscosity evolution with respect to the O-containing components under controlled condition was discussed.

2. Experimental

A specified amount of Tahe heavy oil (20 g) was added into a 100 mL PTFE reactor with different dosage of hydrogen peroxide solution (0, 0.5, 1, 1.5, 2, 4, 6, 8 mL, respectively, 30 wt%). The reactor was heated at 100 °C for 12 h with 50 rpm rolling to undergo the oxidation. After which, the heavy oil samples were taken out to cool down with successive removal of free water. The thermal pyrolysis of these samples was carried out for 24 h at 240 °C under 2 MPa N_2 atmosphere in a FYX-0.5 high-pressure reactor. Elemental analysis for O, S, N, C, H of both original, oxidized and pyrolyzed heavy oil samples was measured three times in parallel in an elemental analysis instrument (EL, VARIO EL-2, Germany) with O pattern and CHNS pattern. After removal of water, the viscosity of oil samples was determined by the Brookfield DV-II+ programmable viscometer on a 29# spindle at 50 °C [30]. The TAN (total acid number, mg KOH/g) was determined by potentiometric titration on a ZDT-4A automatic potentiometric titrator (Shanghai, China) referring to the China standard test method (GB/T 7304-2014). The SARA components (saturated hydrocarbons (SH), aromatic hydrocarbons (AH), resins and asphaltenes) were separated from oil samples by a Al_2O_3 chromatography column according to the industrial standard of China Petroleum NB/SH/T 0509-2010, of which the specific procedure was present in the Supporting information. In addition, the CO_2 volume fraction in the residual gas of original and oxidized oil samples after thermal pyrolysis was tested on a gas chromatography (GC-2014A, SHIMADZU, Japan) with a TCD detector.

The acidic components of the original and oxidized heavy oil samples were extracted via liquid-liquid extraction method. Specifically, 5 g of oil sample was dissolved in 20 mL of n-hexane at 60 °C, then 30 mL of 0.1 M NaOH ethanol solution was added to induce saponification. The acid in oil sample would be transformed to sodium soap, which was extracted by 0.1 M NaOH ethanol solution for three times. Subsequently, the NaOH ethanol solution was neutralize by diluted HCl solution to recover the carboxylic acids. Finally, the carboxylic acids were extracted by methylene chloride and condensed. After which, the acidic components were characterized by Fourier transform infrared spectrometer (FT-IR, Nicolet 5700 spectrometer, USA), carbon nuclear magnetic resonance spectroscopy (^{13}C NMR BRUKER Ascend400, Germany) and gas chromatography-mass spectrometry (GC–MS, Agilent GC7890A-MSD5975C, USA). Before injected into GC instrument, the acidic components were pretreated by 15 wt% BF_3 in methanol solution to be methyl esterified at 70 °C for 1 h, which were extracted by hexane with assistance of ultrasonic wave and concentrated to 0.5 mL for GC–MS analysis. The special heating procedure is programmed to hold the preliminary temperature at 80 °C for 0 min then raise it by 4 °C/min to 160 °C, followed by 3 °C/min to 280 °C for 10 min.

3. Results and discussion

Elemental analysis show that the O content of the oil sample is elevated with the increasing addition of H_2O_2 (Table 1), however, the distribution of C, H, N, S remains almost unchangeable. Fig. 1 displays the TAN and viscosity of the Tahe heavy oil samples before and after

Table 1
Elemental analysis results of original oil sample and oxidized oil samples with different dosage of H_2O_2. (N_H/N_C: atomic ratio of hydrogen to carbon).

Content (wt%)	O	S	N	C	H	N_H/N_C
–	2.61	0.73	0.97	83.26	12.43	1.79
2 mL	2.95	0.73	0.97	83.02	12.33	1.78
4 mL	3.12	0.73	0.96	82.91	12.28	1.78
8 mL	3.43	0.72	0.96	82.66	12.23	1.78
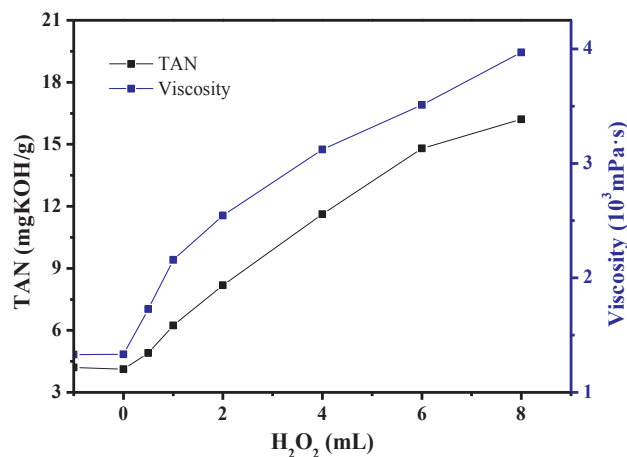
Fig. 1. The viscosity and TAN evolution with respect to the dosage of H_2O_2.

oxidization with different dosage of H_2O_2. For the heavy oil sample without the presence of H_2O_2, both TAN and viscosity after thermal treating at the same temperature and pressure are almost identical to that of original heavy oil, suggesting that no visible component change has occurred during the set oxidizing condition (100 °C, 12 h). The participation of H_2O_2 in the thermal treatment will bring considerable property variations of the heavy oil samples. Within the dosage range, TAN increases quasi-linearly with the adding amount of peroxide, implying that the oxidation would generate large amounts of acidic species. Interestingly, the viscosity of the samples evolves quasi-monotonically from 13300 mPa·s (original heavy oil) to 39694 mPa·s when H_2O_2 dosage is set to be 8 mL (Table S1). A strong positive correlation between the TAN and viscosity can be naturally derived. This is understandable that, the carboxylic acids, generated during oxidation, have strong polarity. These non-hydrocarbon components will easily enter resins or asphaltenes through intermolecular interactions, leading to increment of heavy components. As a consequence, the viscosity of heavy oil should encounter linear increasing trend with respect to the oxidation degree.

We next analyzed the SARA components for selected samples of oxidized heavy oil as well as the original heavy oil, as listed in Table 2. For the employed Tahe heavy oil, we mentioned that the asphaltenes content is ignorable, which indicates that the high viscosity is mainly from resins (49.24 wt%). Although the variation of SH content is almost negligible under different oxidation condition, however, we observed that the AH content encounters gradual drop as the H_2O_2 dosage

Table 2
SARA components of original oil and oil samples oxidized by different dosage (2, 4, 8 mL) of H_2O_2. (SH: saturated hydrocarbons, AH: aromatic hydrocarbons).

H_2O_2 (mL)	SH (wt%)	AH (wt%)	Resins (wt%)	Asphaltenes (wt%)
–	27.98	22.77	49.24	–
2	27.56	18.75	53.69	–
4	27.65	15.74	55.65	0.96
8	27.63	14.06	56.88	1.43