[Research Note]

Effects of Changes in Asphaltenes on Viscosity Reduction of Heavy Oil after Thermal Visbreaking

Yaorong CAI, Ruiming WU, Yan SHI*, Xiaoqiang WANG, Zhiwei YAO, and Qingshan RONG

College of Chemistry, Chemical Engineering and Environmental Engineering, Liaoning Shihua University, Fushun, 113001, P. R. CHINA

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Changes in asphaltene content in heavy oils after thermal visbreaking at different cracking temperatures and reaction times were studied by various techniques, including elemental analysis, X-ray diffraction, Fourier transform infrared spectroscopy and nuclear magnetic resonance spectroscopy. The yield of asphaltene decreased at the beginning of thermal visbreaking, but further increased with deep thermal visbreaking. The aromaticity of asphaltene increased with higher cracking severity. In addition, the effect of asphaltene on viscosity was investigated before and after thermal visbreaking. There was a close relationship between asphaltene content and viscosity, and the viscosity increased dramatically with higher asphaltene content. The viscosities were also different at the same asphaltene content due to the differences in chemical composition and macrostructure of the asphaltene molecules. Therefore, both the contents and structures of asphaltene had significant influences on the viscosity of heavy oils. However, the changes in the content and structure of asphaltene were not major causes for the decrease in viscosity after thermal visbreaking.

Keywords

Heavy oil, Asphaltene, Viscosity, Visbreaking

1. Introduction

Heavy oils are present in huge reserves with world-wide distribution, but have high viscosity greater than 0.1 Pa s¹⁾, which limits both extraction and transportation. Various technologies have been applied to reduce the viscosity^{2)~4)}, including additives to the oil, heating of the oil, blending the oil with lighter oils or hydrocarbon gases, oil-in-water emulsification and microbial methods. Thermal visbreaking has also been widely applied because of the lower capital and operation costs.

Thermal visbreaking is a mild form of thermal cracking in which the viscosity of the heavy oils is permanently decreased by the cleavage of C–C bonds and the opening of ring structures to form a larger number of molecules with lower viscosity. Previous studies of thermal visbreaking have focused on the visbreaking process, changes in the physical and chemical properties of cracked products⁵⁾, reaction pathways or kinetics^{6),7)}. The effect of the fractions from cracked products has not been widely reported. Additionally, the presence of asphaltene is important in the high viscosity of heavy oil. Asphaltene is generally recognized to cause higher

viscosity in different fractions, which originates from the specific properties dependent on the formation of intermolecular aggregates with other hydrocarbons^{1),8)~10)}. Therefore, the effect of asphaltene on viscosity should be understood.

This study investigated the changes in asphaltenes after thermal visbreaking using various methods, including elemental analysis, X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy and nuclear magnetic resonance (NMR). In addition, oil samples were prepared by diluting the asphaltene fraction into *n*-heptane deasphalted oils and determining their viscosity. Finally, the involvement of asphaltene in the decrease of viscosity after visbreaking and the effects of asphaltene on the viscosity of heavy oils were evaluated.

2. Experimental**2.1. Materials**

Experimental heavy oil samples were obtained from MRE-2, Venezuela, and used as the feedstock for thermal visbreaking. Samples were separated into *n*-heptane asphaltenes (MREAP) and *n*-heptane deasphalted oils (DAO). The properties of the feedstocks are shown in **Table 1**. All experimental samples were stirred to ensure homogeneous samples. Other materials included *n*-heptane (97 %) and toluene (97 %) supplied by

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* To whom correspondence should be addressed.

* E-mail: shiyan1816@163.com

Table 1 Properties of MRE-2 Crude Oil

Properties	Value	Distillation [vol%]	T [°C]
$\rho^{25.1\text{ }^{\circ}\text{C}}$	[kg/m ³] 975	0	172
μ	[mPa s, 25 °C] 8775	5	279
Elemental analysis	[wt%]	10	302
C	82.75	20	370
H	13.60	30	439
N	0.53	40	498
S	3.62	50	567
SARA content	[wt%]	60	619
Saturates	28.7		
Aromatics	30.3		
Resins	30.8		
N-C ₇ Asphaltenes	10.3		

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2. 2. Preparation of Asphaltene and Reconstituted Oil Samples

The thermal visbreaking experiments were conducted at three cracking temperatures (370, 390, and 410 °C) and three reaction times (30, 50, and 60 min) in a stainless steel reactor. The liquid products were collected and the cracked oils were separated into asphaltene and deasphalted oil according to ASTM D4124. The asphaltenes were specified as 370/30AP, 370/60AP, 370/90AP, 390/30AP, and so on. Then, the reconstituted oil samples were prepared by diluting asphaltene into the DAO. Firstly, to study the relationship between asphaltene content and viscosity, six reconstituted oil samples containing different asphaltene mass fractions of 2.5, 5.0, 7.5, 10.0, 12.5 and 15.0 wt% were prepared with DAO. Secondly, to investigate the effect of cracked asphaltene on the viscosity of heavy oil, ten reconstituted oil samples containing constant asphaltene mass fraction (10.0 wt%) were prepared. For example, the sample of 37/3AO was prepared by diluting 370/30AP into DAO. The viscosities of these reconstituted oil samples were determined at different temperatures (shear rate from 1 to 200 s⁻¹).

2. 3. Characterization of Asphaltenes

Elemental analysis of the asphaltenes was carried out with a Vario MICRO CUBE analyzer to determine the carbon, hydrogen, nitrogen, and sulfur contents. The oxygen content was calculated by subtracting the C, H, N, and S contents from 100 %.

XRD analysis was carried out with a D-max-RB instrument using 30 kV voltages and 15 mA current, using CuK α (1.5405 Å, 1 Å = 10⁻¹⁰ m) monochromatic energy radiation. A NaI detector (scintillation detector) was used to collect the diffraction signals. The diffraction angle (2 θ) was scanned from 11 to 70° at 1°/min scan rate with a 0.05° step size. According to the XRD patterns with curve de-convolution for asphaltenes (Fig. 1), the aromaticity (f_a) and the average height (L_c) of the stack of the aromatic sheet were calculated from the following equations⁵⁾:

Fig. 1 XRD Pattern of Asphaltene

$$f_a = \frac{A_{(\text{graphene})}}{A_{(\text{graphene})} + A_{(\gamma)}} \quad (1)$$

In Eq. (1), $A_{(\text{graphene})}$ and $A_{(\gamma)}$ are the areas of resolved peaks for the graphene and γ bands, respectively.

$$L_c = 0.9 \omega \cos \theta_{002\text{-band}} \quad (2)$$

In Eq. (2), $\theta_{002\text{-band}}$ and ω are the Bragg's angle at which the peak of (002) band is centered and the band-width, respectively.

The changes in asphaltene after thermal visbreaking were investigated by Fourier transform infrared (FT-IR)

Fig. 2 FT-IR Spectra of Asphaltene

spectrometry (Perkin-Elmer USA). The spectra was recorded in the range of 400-4000 cm^{-1} , with a resolution of 0.482 cm^{-1} . The FT-IR spectrum of asphaltene sample is shown in **Fig. 2**. The peak areas A_1 , A_2 and A_3 were calculated by computer software, which corresponded to the aliphatic CH (3000-2800 cm^{-1}), carbonyl C=O (1770-1650 cm^{-1}) and aromatic C=C (1650-1550 cm^{-1}) stretching absorption regions respectively¹¹.

The carbon aromaticities of asphaltene were determined with a 300 MHz NMR spectrometer (Mercury-300, Varian, USA). Asphaltene samples were dissolved into deuterated chloroform (CDCl_3) and the NMR spectrometer was preset with a pulse flip angle of 30°, sampling tube diameter of 5 mm, and spectral width of 15 ppm and 235 ppm for measuring the ^1H NMR spectra and ^{13}C NMR spectra, respectively. Intensity after the integration process was used for the calculation of aromaticity. According to ASTM D5292-99, the aromaticity, f_a , of the asphaltene sample was calculated as follows:

$$f_a = \frac{A}{A + B} \quad (3)$$

A and B refer to the integrals for the aromatic hydrogen band (5.0-10.0 ppm region) and aliphatic hydrogen band (0.3-5.0 ppm region) from ^1H NMR spectra and ^{13}C NMR spectra, respectively. For the aromatic hydrogen content, A and B are equal to the integrals for the aromatic hydrogen band (5.0-10.0 ppm region) and aliphatic hydrogen band (−0.5-5.0 ppm region), respectively. For the aromatic carbon content, A and B are equal to the integrals for the aromatic carbon band (100-170 ppm region) and aliphatic carbon band (−10-70 ppm region), respectively. Sample ^1H and ^{13}C NMR spectra of MREAP are presented in **Figs. 3** and **4**, respectively.

3. Results and Discussion

3.1. Changes in Asphaltene

The elemental compositions and contents of asphal-

(a)

(b)

Fig. 3 ^1H NMR Spectra of MREAP (a) and 390/30AP (b)

(a)

(b)

Fig. 4 ^{13}C NMR Spectra of MREAP (a) and 390/30AP (b)

Table 2 Elemental Composition and Yield of Asphaltene

	MREAP	370			390			410		
		30	60	90	30	60	90	30	60	90
Yield [%]	10.5	9.8	10.2	11.9	9.6	10.8	12.3	9.7	11.5	13.2
Element content [%]										
C	81.5	83.2	84.2	85.0	83.8	84.8	85.3	84.0	85.0	85.5
H	9.4	9.0	8.8	8.7	8.9	8.8	8.6	8.7	8.6	8.5
O (differ.)	2.0	1.0	1.8	1.1	1.5	1.4	1.4	1.0	1.2	1.0
N	2.6	2.5	2.0	1.6	1.9	1.8	1.5	2.6	1.8	1.7
S	4.5	4.3	3.8	3.6	3.9	3.5	3.2	3.7	3.4	3.3

Table 3 Aromaticity (f_a) and Average Height (L_c) of the Stack of the Aromatic Sheet from XRD

Asphaltene	MREAP	370/30AP	370/60AP	370/90AP	390/30AP
f_a	0.01	0.01	0.02	0.03	0.03
L_c [Å]	21.5	23.8	20.7	15.4	22.8
Asphaltene	390/60AP	390/90AP	410/30AP	410/60AP	410/90AP
f_a	0.04	0.08	0.05	0.07	0.09
L_c [Å]	20.3	19.9	22.2	19.5	18.8

Table 4 Aromaticity (f_a) of Asphaltene from NMR Analysis

Asphaltene	MREAP	370/30AP	370/60AP	370/90AP	390/30AP
^1H aromaticity	0.16	0.17	0.18	0.20	0.19
^{13}C aromaticity	0.35	0.36	0.36	0.38	0.36
Asphaltene	390/60AP	390/90AP	410/30AP	410/60AP	410/90AP
^1H aromaticity	0.19	0.21	0.18	0.20	0.22
^{13}C aromaticity	0.37	0.39	0.36	0.37	0.40

tene in MRE-2 and cracked products are shown in **Table 2**. Clearly the yield of asphaltene decreases at the beginning of thermal visbreaking due to the breaking of the weak bonds between alkyl groups and the poly-aromatic base unit. Subsequently, the yield of asphaltene increases with deep thermal visbreaking because the asphaltenes and maltenes undergo other reaction pathways, such as dehydrogenation, aromatization of naphthenic groups, condensation or pericondensation of aromatic rings, and so on. In addition, the content of C increased but the content of H decreased with deep thermal visbreaking. The changes of content of other elements are difficult to determine. The results indicate that the aromaticity of asphaltene increases with higher cracking severity.

XRD analyses of the changes in aromaticity (f_a) and average height (L_c) of the stack of the aromatic sheet are shown in **Table 3**. Aromaticity (f_a) increased but average height (L_c) of the stack of the aromatic sheet decreased with higher temperature and longer reaction time. The aromaticity (f_a) and the average height (L_c) of the stack of the aromatic sheet are dependent on the severity of thermal visbreaking⁵.

NMR analyses of the ^1H and ^{13}C aromaticity (f_a) of

various asphaltenes are shown in **Table 4**. ^1H and ^{13}C aromaticity (f_a) depended on the reaction temperature and time in agreement with the XRD findings. However, the values from XRD are smaller than from NMR because the calculation of aromaticity (f_a) from the XRD spectra is based only on the stack cluster aromatic carbon which contributes to the graphene peak rather than all aromatic carbon in the asphaltene.

The A_3/A_1 (degree of aromaticity in the molecular matrix) and the A_2/A_3 ratio (degree of carbonyl concentration per unit of aromatic structures) were considered¹¹⁾ as listed in **Table 5**. The A_3/A_1 and A_2/A_3 ratios displayed complex trends due to the asphaltenes undergoing primary and secondary reactions.

3.2. Variation in Viscosity after Visbreaking

The viscosities of thermal visbreaking products are compared in **Fig. 5**. The viscosity of cracked oil decreased with longer reaction time and higher reaction temperature. The decrease in viscosity is ascribed to the changes in the chemical composition of the oil after thermal treatment.

3.3. Viscosity and Asphaltene

The relationship between viscosity and asphaltene content at different temperatures is shown in **Fig. 6**.

Table 5 Changes Aromaticity in the Molecular Matrix (A_3/A_1) and Carbonyl Concentration per Unit of Aromatic Structures (A_2/A_3)

Asphaltene	MREAP	370/30AP	370/60AP	370/90AP	390/30AP
A_3/A_1	0.14	0.17	0.10	0.18	0.20
A_2/A_3	0.21	0.28	0.89	0.12	0.20
Asphaltene	390/60AP	390/90AP	410/30AP	410/60AP	410/90AP
A_3/A_1	0.13	0.13	0.16	0.08	-
A_2/A_3	0.52	0.39	0.47	1.01	1.01

Table 6 Effect of Cracked Asphaltene on Viscosity of Heavy Oil

Oil sample (asphaltene content = 10 wt%)	MREAO	37/3AO	37/6AO	37/9AO	39/3AO
Viscosity [mPa s, 25 °C]	7665	10001	19472	18972	13645
Oil sample	39/6AO	39/9AO	41/3AO	41/6AO	41/9AO
Viscosity [mPa s, 25 °C]	11134	18140	14598	15318	25872

MREO refers to feedstock, and others refer to the products of thermal visbreaking, such as 390/30 (products of visbreaking at 390 °C for 30 min).

Fig. 5 Changes in Product Viscosity at 25 °C after Thermal Visbreaking

The viscosity of reconstituted oil increased with higher asphaltene content at constant temperature (especially at 25 °C). However, a critical mass fraction (about 10 wt%) of asphaltene existed between asphaltene content and viscosity of reconstituted oils. Asphaltene content is above 10 wt% resulted in dramatically increased viscosity due to the agglomeration of asphaltene particles and strong inter-particle interactions between these asphaltene particles.

The effects of cracked asphaltene on viscosity of heavy oil are compared in **Table 6**. The viscosity of cracked asphaltene reconstituted oil samples was higher than that of MREAO at 25 °C, and the change in viscosity of reconstituted heavy oil sample showed no trend. According to present suspension viscosity theories, the volume fraction and aggregation state of asphaltene particles in any heavy oil sample can greatly affect its viscosity. The unstable changes in viscosity result from the complex reactions of asphaltene, including

Fig. 6 Relationship between Asphaltene Content and Viscosity

dealkylation of side aliphatic chains, cyclization of alkyl chains, and combination of ring radicals by polymerization, dehydrogenation and aromatization of naphthenic rings, and condensation and pericondensation of aromatic rings.

4. Conclusion

The effects of the content and structure of asphaltene on the viscosity of heavy oil were investigated. The structure of asphaltene was characterized by elemental analysis, XRD, NMR and FT-IR. The structure and contents of asphaltene were changed by thermal visbreaking, and were significant in the changes in viscosity, but not the major reason for viscosity reduction.

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