Impact of Aging on Molecular Structure of Asphalts from Different Crude Oils

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Reference

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ABSTRACT

This research aimed to explore the impact of aging on the molecular structure of asphalts from different crude oils. The elemental composition of five types of original asphalts was measured. The structure changes of the asphalts were analyzed with Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (^{1}H-NMR) before and after thin-film oven test, ultraviolet light (UV), and pressure aging vessel (PAV). The result of the elemental analysis showed that the hydrogen-carbon ratio (H/C) of asphalts ranges from 1.347 to 1.602 with different contents of sulfur, nitrogen, and oxygen. The FTIR indicated that asphalts with a low H/C had a low rate of change of carbonyl index after aging. Asphalts were more likely to produce an aromatic ring structure and sulfoxide group during the PAV aging process. The aliphatic structure was easier to reduce during the UV aging process. The ^{1}H-NMR analysis showed that the content of aromatic hydrogen (H_{ar}) of asphalts is between 0.022 and 0.056, the content of H_{ar} decreased after aging, and the asphalt with a low H_{ar} content had a smaller change rate of hydrogen atom content. The outlined research results revealed that the asphalt with lower H/C and H_{ar} content was prone to have better aging resistance.

Keywords

asphalt, aging, molecular structure, Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (^{1}H-NMR)

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Introduction

Asphalt pavement is widely used owing to its advantages such as comfortable driving, low noise, short construction cycle, and recyclability.[1] As a material mainly composed of carbon and hydrogen atoms, asphalt is susceptible to aging because of oxygen, heat, ultraviolet light (UV), etc., which deteriorate its performance.[2–5] These changes are the external manifestation of composition, molecular structure, and transformation of asphalt.[6,7] Therefore, the research on the effect of aging on molecular structure of asphalt is helpful for understanding the aging mechanism of asphalt and is vital for selecting asphalt used for pavement.

The aging process of asphalt is complex. A lot of research has done on asphalt aging, mainly focused on the changes of macro-performance before and after aging.[8] Based on the changes of physical or rheological properties, the influence of aging on properties of asphalt was analyzed. The findings revealed that although various asphalts had different aging resistances, the variation trend of their properties after aging was consistent. The asphalt showed an increase in high-temperature stability, a decrease in low-temperature crack resistance, and a weakening of fatigue performance after aging.[9–12]

With the advanced characterization approaches, many scholars explored the aging mechanism of asphalt by analyzing changes in molecular structure. Gel permeation chromatography (GPC) can determine a polymer's molecular weight and its distribution and quantitatively analyze molecular weight changes of asphalt during the aging process. Herrington, Patrick, and Ball[13] explored the thin-film oven test (TFOT) aging mechanism by GPC and found that the molecular weight distribution and average molecular weight increased significantly after the aging. Liu et al.[14] analyzed aging resistance of asphalt from different crude oils during TFOT and pressure aging vessel (PAV) aging using GPC and Fourier transform infrared spectroscopy (FTIR). The result showed that asphalt with a high saturate fraction and asphaltene content, large activation energy, and small reaction rate coefficient had a better antiaging performance.

FTIR allows a finer characterization of the functional groups of asphalt. It is used to analyze asphalt heteroatom groups, aromatic structures, etc., in the study of asphalt aging. Lamontagne et al.[15] conducted a detailed analysis of the absorption peaks around 1,700 cm^{-1} and found that the main products were carboxylic acids and ketones in the aging process of asphalt. Li et al.[16] characterized UV aged asphalt by FTIR and X-ray photoelectron spectroscopy. It showed that the oxygen-containing functional group content of the aged asphalt was higher than that of the original asphalt. Ye et al.[17] investigated the TFOT aging mechanism of asphalt based on FTIR. The result showed that as the temperature increased, both oxidation and volatilization were accelerated and oxidation was less sensitive to temperature than volatilization. Soenen, Lu, and Laukkanen[18] characterized asphalt structure by FTIR and UV visible spectra after PAV aging and air-blowing aging. They found that larger conjugated aromatic compounds were formed after aging. Nuclear magnetic resonance spectroscopy (NMR) can distinguish the chemical environments of hydrogen and carbon atoms. Based on the chemical shift and peak area of the peak in the spectrum, the type and corresponding content of hydrogen or carbon atoms are obtained, and the molecular structure of asphalt is analyzed. Nciri et al.[19] compared the ^{13}C-NMR of Gilsonite and Lake Trinidad asphalt. Compared with Gilsonite, there were more oxygen-containing compounds and proton-containing aromatic compounds in Lake Trinidad asphalt, and its alkyl chain was easier to oxidize and sulfide. Nciri and Cho[20] analyzed the different types of hydrogen content in petroleum asphalt and natural asphalt by ^{1}H-NMR and found that the aliphatic hydrogen content in natural asphalt was higher than that in petroleum asphalt, indicating that natural asphalt contained more highly branched molecules. Siddiqui[21] used ^{1}H-NMR to analyze the molecular structure of asphalt fractions after TFOT and PAV aging and found that the asphalt underwent isomerization and dehydrogenation reactions.

The existing research mainly focused on the structure changes of the same asphalt before and after thermal oxidative aging. But few studies investigated the effects of aging on the molecular structure of asphalts from different crude oils. However, the molecular structure of asphalts from different crude oils varies greatly,[22] and the UV aging also has a great impact on the structure of asphalts. Therefore, the purpose of this paper is to study the impact of aging on the molecular structure of asphalts from different crude oils. Five different types of asphalts of the same grade were selected to suffer from TFOT, PAV, and UV aging. The elemental analysis, FTIR, and ^{1}H-NMR were used to determine the elemental composition, functional group, and chemical structure during the aging process.

Materials and Methods

MATERIALS

This study was conducted on five different asphalts with the same penetration grade of 60/80. The physical properties of these asphalts were listed in **Table 1**. The penetration, softening point, and viscosity were tested according to standard ASTM D5/D5M-20, *Standard Test Method for Penetration of Bituminous Materials*, ASTM D36/D36M-14(2020), *Standard Test Method for Softening Point of Bitumen (Ring-and-Ball Apparatus)*, and ASTM D4402/D4402M-15, *Standard Test Method for Viscosity Determination of Asphalt at Elevated Temperatures Using a Rotational Viscometer*, respectively.

AGING PROCEDURE

TFOT Aging

The TFOT aging was utilized to simulate short-term aging of asphalts during conventional hot-mixing. The asphalt was aged by the TFOT test according to the standard ASTM D1754/D1754M-20, *Standard Test Method for Effects of Heat and Air on Asphaltic Materials (Thin-Film Oven Test)*, and the test duration and temperature were 5 h and 163°C, respectively.

PAV Aging

According to ASTM D6521-19a, *Standard Practice for Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel (PAV)*, the PAV aging was operated to simulate long-term ageing. This test is conventionally assumed to reproduce the aging occurring during the service life. During the PAV aging process, the aged asphalt samples from the TFOT test were heated in a PAV with a pressure of 2.1 MPa at 100°C for 20 h.

UV Aging

In order to simulate the photooxidative aging occurring in service life, the asphalt samples treated with TFOT were then placed into the ultraviolet radiation oven for 10 days.[23,24] The temperature of the UV aging was 60°C. The UV radiation was 2,000 $\mu W/cm^2$, and the UV lamp power was 500 W.

CHARACTERIZATION

Elemental Analysis

The elemental composition of asphalts before and after aging was characterized using an elemental analyzer (Vario EL cube, Germany). The quality of asphalt samples was controlled at 5±1 mg. The content of carbon, hydrogen, nitrogen, and sulfur in asphalt (mass fraction, the same below) was obtained through analysis and detection, and the analysis accuracy was less than 0.1 %. Considering that the contents of other components such as iron and nickel in asphalt are all at the parts per million level, they have little effect on the oxygen content. The content of oxygen is calculated by the subtraction method. The hydrogen-carbon ratio (H/C) is used to characterize the chemical composition of asphalt, and the H/C can reflect the average molecular structure of asphalt to some extent.[19]

TABLE 1

Properties and crude oil of the asphalt samples

Asphalt	Penetration, 25°C, 0.1 mm	Softening Point, °C	Viscosity, 60°C, Pa•s	Oil Source
A1	66	49.5	333	Cold lake crude oil
A2	66	48.0	247	Kuwait crude oil
A3	64	47.0	202	Huanxiling crude oil
A4	69	49.0	283	South America crude oil
A5	67	49.0	273	Kabinda crude oil

FTIR

The functional groups of asphalts before and after aging were characterized using FTIR (Thermo Scientific Nicolet iS50, USA). Firstly, the asphalt was dissolved into carbon disulfide with a concentration of 5 % wt. Then, the solution was dropped on the potassium bromide thin plate and irradiated by mercury lamp. Finally, FTIR test were conducted at the range of 400–4,000 cm^{-1}. The instrument resolution and scanning times were set at 4 cm^{-1} and 64 times, respectively.

The aromaticity index (I_{Ar}), the aliphatic index (I_{Ali}), the carbonyl index ($I_{C=O}$), and the sulfoxide index ($I_{S=O}$) were employed to quantify the impact of aging on the chemical structure of asphalt. The structural and functional indexes are calculated with equations[25,26] (1)–(5).

$$I_{\text{Ar}} = \frac{A_{1,600}}{\sum A} \tag{1}$$

$$I_{\text{Ali}} = \frac{A_{1,460} + A_{1,376}}{\sum A} \tag{2}$$

$$I_{C=O} = \frac{A_{1,700}}{\sum A} \tag{3}$$

$$I_{s=o} = \frac{A_{1,030}}{\sum A} \tag{4}$$

$$\sum A = A_{(2,953,2,862)} + A_{1,700} + A_{1,600} + A_{1,460} + A_{1,376} + A_{1,030} + A_{864} + A_{814} + A_{743} + A_{724} \tag{5}$$

where A_i is the peak area corresponding to wave number i.

^{1}H-NMR

The molecular structure of asphalts before and after aging was characterized using ^{1}H-NMR (A Bruker AVANCE III HD, Switzerland). This experiment was conducted in two steps: First, the deuterium chloroform was used as the solvent. Six mg of asphalt were dissolved into 6 ml of solvent and left for enough time to dissolve completely. Second, the solution was dropped into a nuclear magnetic tube with a glass dropper. The tube was then covered with a cap, and this test was performed with tetramethylsilane as the internal standard.

The schematic diagram of proton attribution is shown in **figure 1**.[27] The division and assignment of the ^{1}H-NMR spectrum are shown in **Table 2**.[27] By analyzing the content of hydrogen atoms, the chemical structure of asphalt can be observed.

FIG. 1

The schematic diagram of attribution of H_α, H_β, H_γ, and H_{ar}.

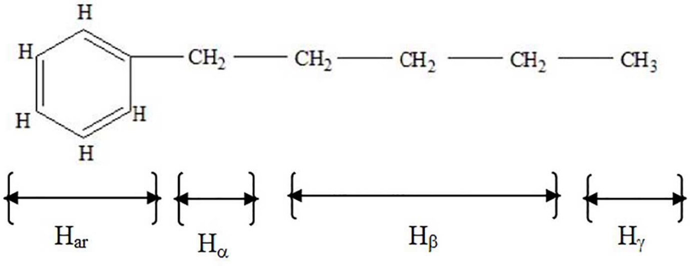


TABLE 2

Types of protons in ^{1}H-NMR spectrum

Parameter	Chemical Shift, ppm	Types of Protons
H_α	2.0–4.0	Aliphatic hydrogen on C_γ to aromatic rings
H_β	1.0–2.0	Aliphatic hydrogen on C_β and the CH_2, CH, beyond the C_β to aromatic rings
H_γ	0.5–1.0	Aliphatic hydrogen on C_γ and the CH_3 beyond the C_γ to aromatic rings
H_{ar}	6.0–9.0	Aromatic hydrogen

Results and Discussion

ELEMENTAL ANALYSIS

The elemental content of five types of asphalts is shown in **Table 3**. It could be seen from **Table 3** that hydrogen content of asphalts ranged from 9.80 % to 10.98 %. The carbon content of asphalts varies between 82.23 % and 87.33 %. A3 had the highest carbon content. But the content of oxygen, nitrogen, and sulfur was significantly different. The sulfur content of A3 was much lower than that of the other four types of asphalt. A2 and A5 contained less oxygen than the other three types of asphalt.

The H/C of asphalts was between 1.347 and 1.602. The order of H/C of asphalts from smallest to largest is A3, A2, A1, A5 and A4. The higher the H/C of the asphalt, the more long-chain structures there are in the asphalt. The lower H/C is, the more ring structures and aromatic structures there are in asphalt.[28,29] It showed that A3 has the highest condensation degree and more aromatic ring structure. A4 had a relatively high H/C and had the lowest degree of condensation and more chain structures.

FTIR ANALYSIS

The FTIR spectrums of all asphalts before and after aging are shown in **figure 1**. As can be seen from **figure 1**, for the original asphalts, there is a characteristic peak near 1,030 cm^{-1}, namely the existence of a sulfoxide group. The spectrum of A3 has a peak of 1,700 cm^{-1}, which belongs to the C=O bond stretching vibration. For aged asphalts, a peak of 1,700 cm^{-1} appeared in the spectrum. The difference between the original, TFOT, UV, and PAV samples was the strength of the peak.

The structural and functional indexes of original, TFOT, PAV, and UV aged asphalt are shown in **figure 2**. There are obvious differences in the indexes of the original asphalts from different crude oils. The aliphatic index of asphalt ranges from 0.2723 to 0.4084. A5 has the largest aliphatic index, while A3 has the smallest aliphatic index. The aromatic index ranges from 0.0510 to 0.0687. The sulfoxide index of A2 is the largest (0.0236), but the sulfoxide index of A3 is only 0.0075, which is one third that of A2.

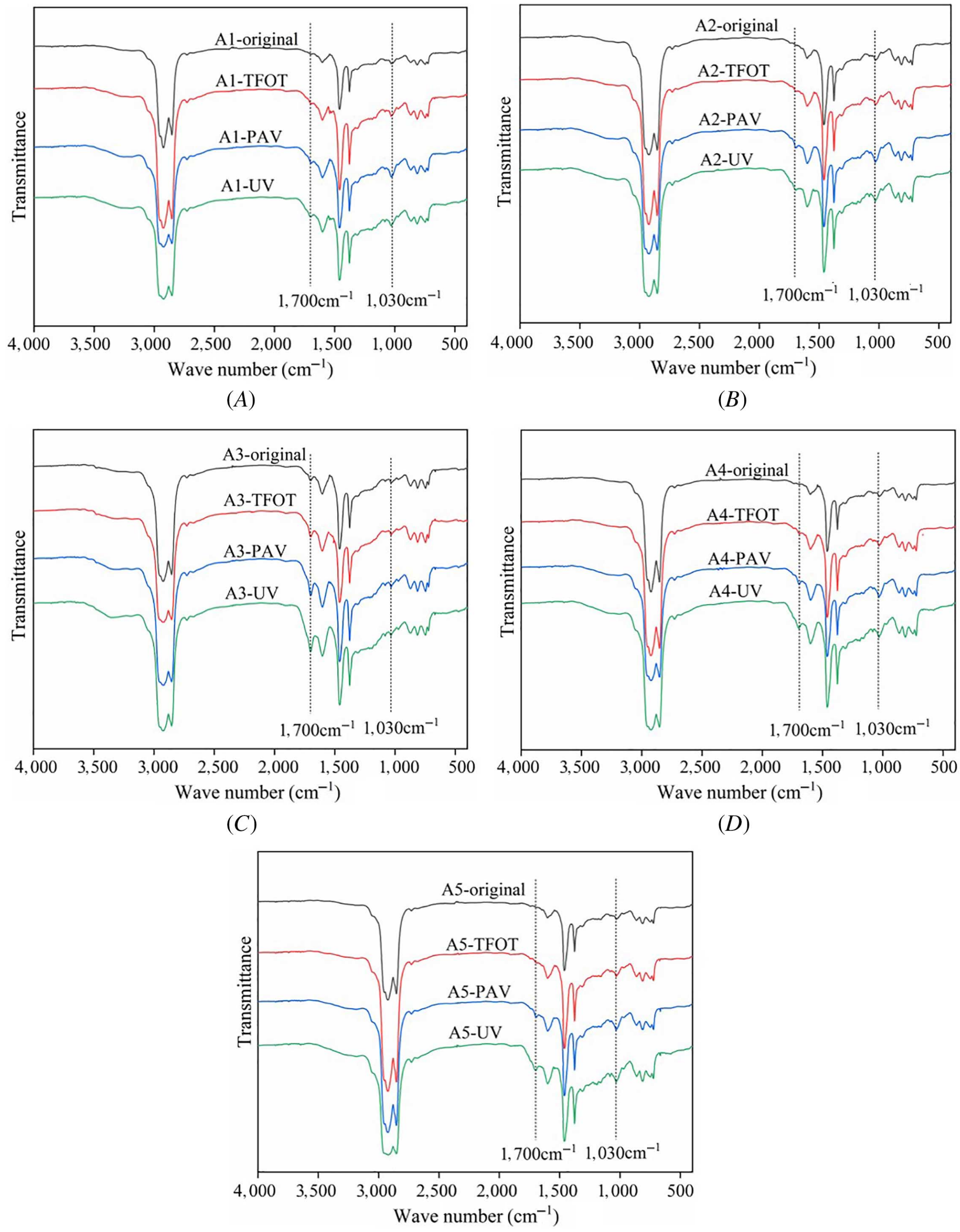
Figure 3*A* and ***3B*** reflected that the aliphatic index of asphalts decreased, and the aromatic index of asphalts increased in the TFOT, PAV, and UV aging processes. It could be seen that the changes in aliphatic index and aromatic index were related. Aging caused an increase in the formation of aromatic structure, but it resulted in reduction of aliphatic structure. The formation of the aromatic structure of asphalt could be attributed to the aromatization of alkyl-substituted naphthenic rings and aromatization of perhydro aromatic rings.

TABLE 3

The elemental composition of asphalts

Asphalt	C %	H %	N %	S %	O %	H/C
A1	82.51	10.41	0.47	5.55	1.06	1.514
A2	82.43	10.08	0.45	6.17	0.87	1.467
A3	87.33	9.80	0.92	0.84	1.11	1.347
A4	82.23	10.98	0.65	4.98	1.16	1.602
A5	82.76	10.85	0.47	5.17	0.75	1.573

FIG. 2 FTIR spectrums of asphalts before and after aging: (*A*) A1, (*B*) A2, (*C*) A3, (*D*) A4, and (*E*) A5.



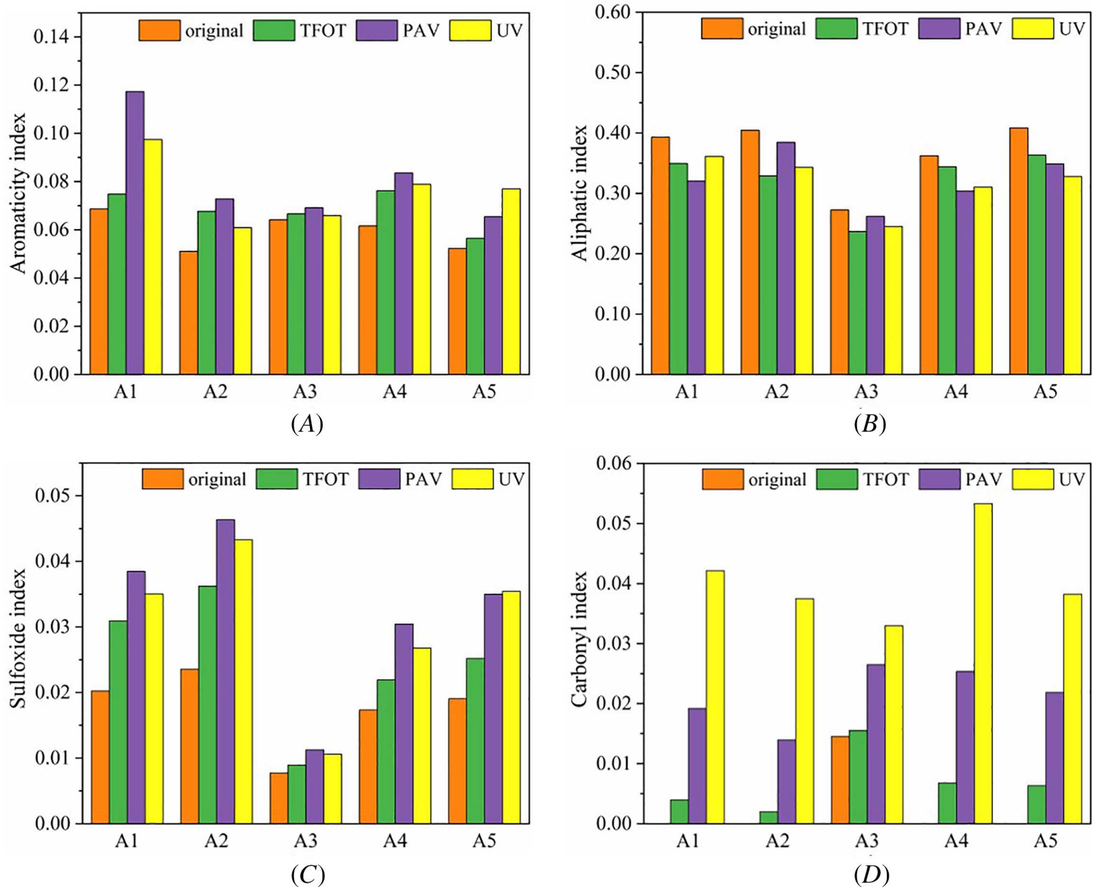
(*A*) (*B*)

(*C*) (*D*)

(*E*)

Figure 3*C* and 3*D* reflected the change of the carbonyl and sulfoxide index. The carbonyl and sulfoxide index of asphalt had an obvious increment after aging, implying that the oxidation reaction occurred in the aging condition. In addition, figure 2*C* showed that the order of sulfoxide index of aged asphalt was the same as that

FIG. 3 The structural and functional indexes of asphalt before and after aging: (*A*) aromaticity index, (*B*) aliphatic index, (*C*) sulfoxide index, and (*D*) carbonyl index.



of original asphalt, which was consistent with the order of sulfur content, indicating asphalt with higher sulfur content produced more sulfoxide groups after aging.

To evaluate the impact of aging on the chemical structure of various asphalts, the change rate or increment of the structural index was calculated by equations (6) and (7). Equation (6) corresponds to the calculation of the change rate (W) of the aliphatic, sulfoxide, and aromatic index. Equation (7) corresponds to the increment (L) of the carbonyl index.

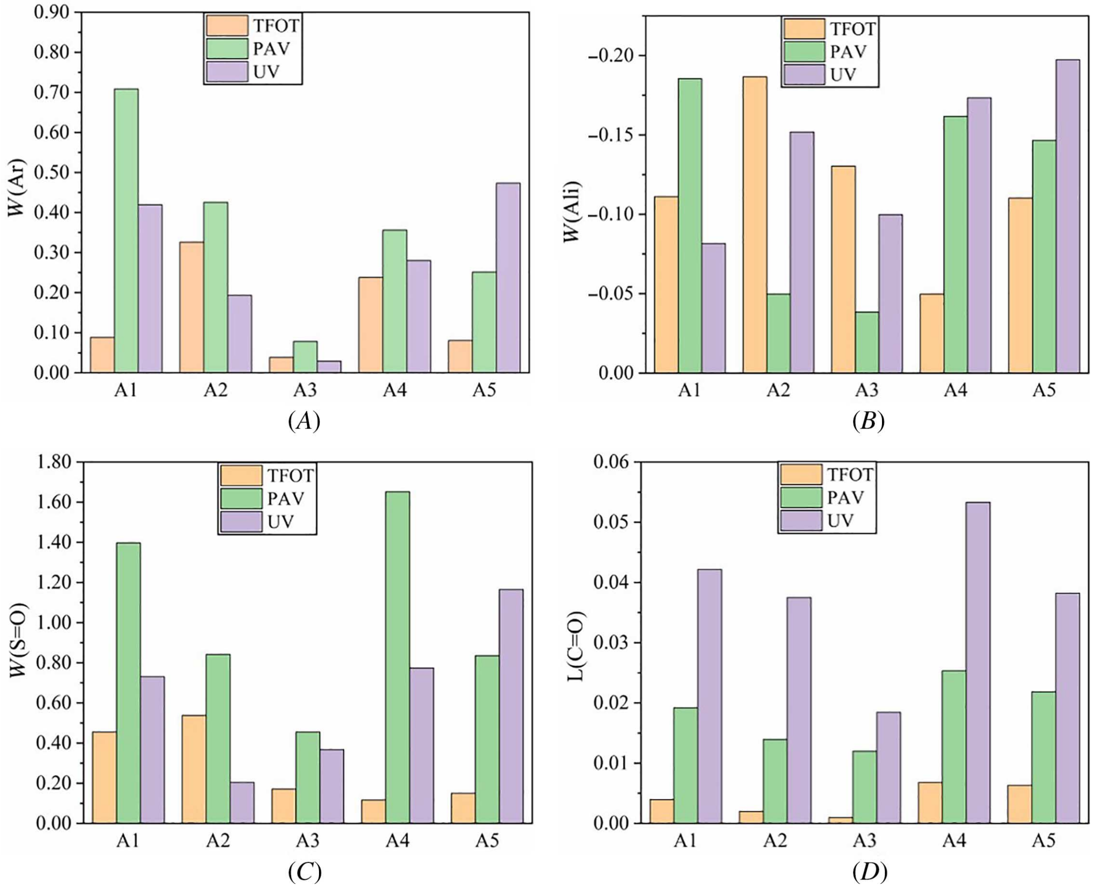
$$W = (I_{\text{aged}} - I_{\text{original}})/I_{\text{original}} \tag{6}$$

$$L = I_{\text{aged}} - I_{\text{original}} \tag{7}$$

where I is the functional and structural indexes.

The change rate or increment of the functional and structural indexes were shown in **figure 4**. **Figure 4*A*** showed that aromatic index of asphalts increased by 3.9–32.6 % after TFOT aging. The aromatic index of A3 increased from 0.0641 to 0.666, and its rate of change was the smallest, while the change rate of A2 was the largest during TFOT aging process, indicating that aromatization of alkyl-substituted naphthenic rings of asphalt occurred. After PAV aging, the change rate of the aromatic index varied greatly. The aromatic index of A1 increased

FIG. 4 Change rate or increment of functional and structural indexes of asphalt: (*A*) change rate of aromaticity index, (*B*) change rate of aliphatic index, (*C*) change rate of sulfoxide, and (*D*) increment of carbonyl index.



from 0.0687 to 0.1173, and it showed the largest increase, while the change rate of the aromatic index of A3 was the smallest. During the UV aging process, the change rate of the aromatic index of A3 was the smallest (2.9 %), and the change rate of A5 was the largest (47.3 %). Comparing change rates of aromatic indexes of asphalts after PAV and UV aging, the change rate of A1, A2, A3, and A4 in the PAV aging process was higher than that of UV aging, which meant that asphalt was more likely to produce an aromatic ring structure in the PAV aging process.

Figure 4*B* showed that the aliphatic index of asphalts decreased by 5–18.7 % after TFOT aging. The change rate of the aliphatic index of A4 was the smallest, but the change rate of A2 was the largest. In the PAV aging process, the aliphatic index of A3 had the minimum change of 3.8 %, and the maximum change rate of A1 was 18.5 %. During the UV aging process, the aliphatic index of asphalts decreased by 8.12–19.7 %. A1 was the smallest but that of A5 was the largest. Comparing the aliphatic index change rate of the five asphalts, the change rate of aliphatic index in the UV aging condition was larger than that in the PAV aging condition. It indicated that the aliphatic structure was more sensitive to UV. Longer alkyl side chains were broken to form low-molecular volatiles, and alkyl side chains were dehydrogenated and condensed. It led to the increase of aromatic structure and the decrease of aliphatic structure.

Figure 4*C* showed that the sulfoxide index of asphalts increased by 11.7–53.8 % and 45.5–165.2 % after TFOT and PAV aging, respectively, and the change rate of the sulfoxide index of A3 was the smallest. After UV aging, the sulfoxide index of asphalt increased by 36.8–85.8 %, with the sulfoxide index of A3 changing the least and the sulfoxide index of A5 changing the most. Comparing the change rate of sulfoxide index after PAV and UV aging, the change rate of the sulfoxide index after PAV aging was larger than that after UV aging, which meant that asphalt was more likely to produce the sulfoxide group during UV aging. Combined with elemental analysis, it could be found that the order of the change rate of the sulfoxide index of the asphalt after aging was consistent with the sulfur content of the original asphalt. The original asphalt with a high sulfur content had more opportunities to react with oxygen during the aging process. As a result, the asphalt generated more of the sulfoxide group, and the sulfoxide index changed greatly.

Figure 4*D* showed that the carbonyl index of asphalt increased by 0.1–0.7 % and 1.2–2.5 %, respectively, after TFOT and PAV aging. The change rate of the carbonyl index of A3 was the smallest, followed by A2, A1, and A5, and the change rate of A4 was the largest. After UV aging, the carbonyl index of asphalt increased by 1.8–5.3 %, and the change rate of A3 was the smallest, while the change rate of A4 was the largest. The results of previous literature indicate that the carbonyl index can be utilized to judge the aging extent of asphalt.[30,31] According to the change rate of the carbonyl index, the aging resistance of A3 is better than other asphalts. Combined with the elemental analysis, it can be found that the order of the change rate of asphalt after aging was consistent with the order of the H/C of the original asphalt; that is, asphalt with a low H/C had little change of the carbonyl index and good antiaging ability. This may be because of the low H/C of asphalt. The asphalt with a low H/C has more ring and aromatic structures, so the asphalt properties are more stable.

The comparison of the change rate of structural index of five asphalt showed that the change rate of the parameters of A3 was relatively small before and after aging, which indicated that the A3 has the stronger anti-aging ability.

^{1}H-NMR SPECTRUM ANALYSIS

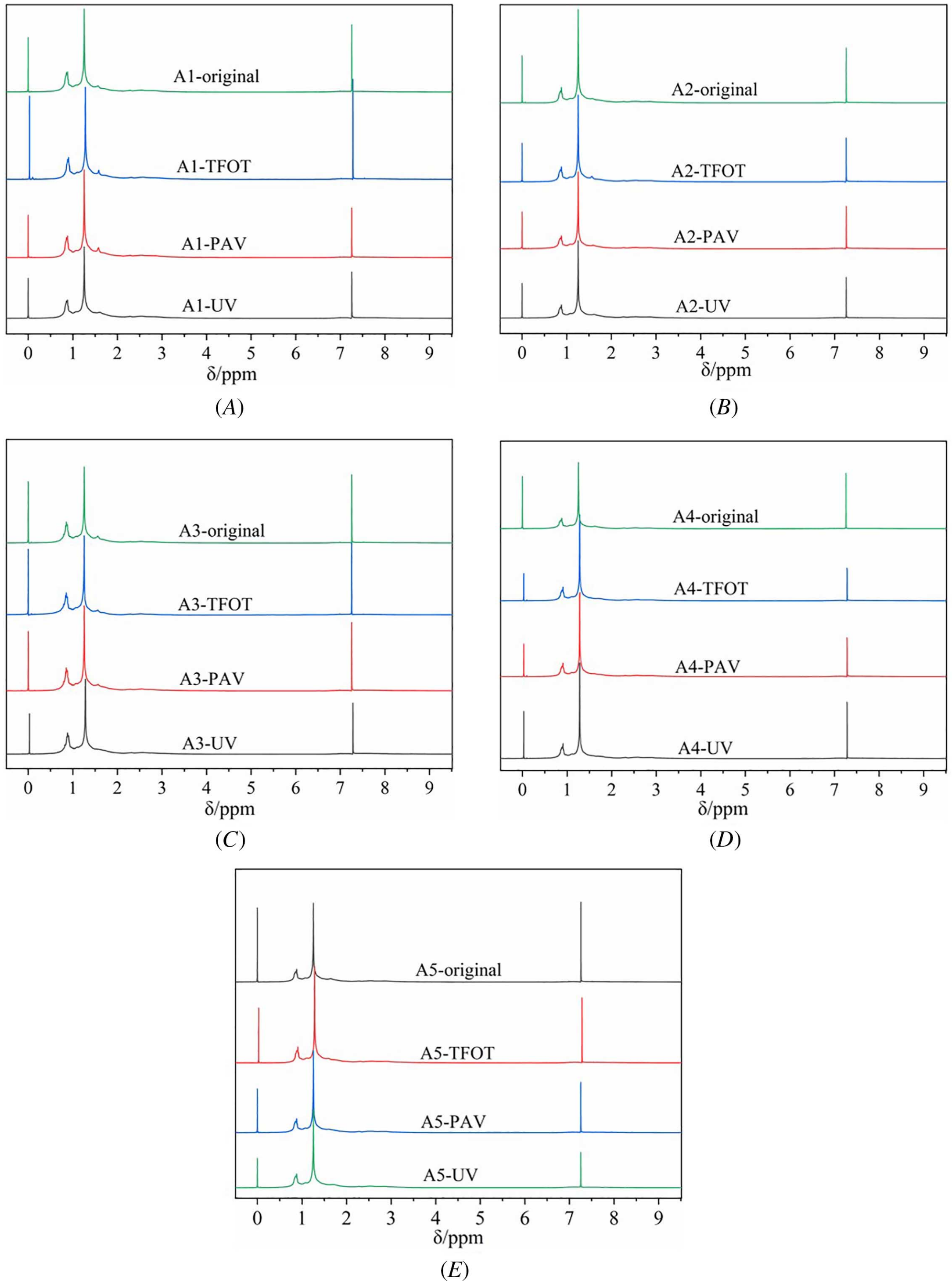
The ^{1}H-NMR spectrums of all asphalts are shown in **figure 5**. It could be seen that positions of hydrogen absorption peaks of original asphalt are similar, and the peak intensities in the aromatic region and partial aliphatic region are different. The ^{1}H-NMR spectrums of asphalts showed that the peak position shifted and the peak area changed after aging.

The percent hydrogen distribution of all asphalt samples was given in **figure 6**. **Figure 6** showed that there was a significant difference in the content of hydrogen atoms in asphalt produced from different crude oil. Among the four different types of hydrogen, the content of H_β is the largest, followed by H_γ and H_α, and the smallest content was in aromatic hydrogen (H_{ar}). It showed that there are a lot of aromatic rings and cycloalkanes in asphalt. The main form of the aromatic system in an asphalt molecule is condensed aromatic ring with a side chain. The longer side chain is the reflection of the higher H_β value.

The H_{ar} content of A4 was the largest, but the H_{ar} content of A3 was the smallest, which indicated that A4 had the lowest aromatic condensation and A3 had the highest condensation. Comparing the H/C of the original asphalt, the order of magnitude of H/C of asphalts was the same as that of H_{ar} content, indicating that the two parameters were consistent in characterizing the asphalt structure. A2 had the lowest H_γ content, which meant that the alkyl side chain in the sample was smaller and shorter. A4 asphalt had the highest H_γ content, containing more long-chain aliphatic hydrocarbons.

Figure 6*A* showed that the H_{ar} content of asphalts decreased after aging, indicating that the aromatic structure underwent condensation dehydrogenation and the degree of condensation increased during the aging process. During the TFOT aging process, the H_{ar} content of asphalts decreased from 57.2 % to 23.3 %. The H_{ar} content of A3 decreased from 0.0219 to 0.0168 (the smallest change), while The H_{ar} content of A5 decreased from 0.0490 to 0.0210 (the largest change), indicating that A5 was more prone to dehydrogenation and condensation during aging. This might be because of its high H_{ar} content and low degree of condensation before aging. After PAV and UV aging, the H_{ar} content of asphalt decreased by 25.6–58.5 % and 38.9–70.3 %, respectively. The change rate of H_{ar} content of A3 was the smallest, which may be because of its low aromatic hydrogen content and a higher degree of condensation before aging. Comparing the H_{ar} content of the five asphalts after aging, the H_{ar} content after TFOT aging was higher than the H_{ar} content after PAV aging, and the H_{ar} content after UV aging was the lowest.

FIG. 5 ^{1}H-NMR spectrums of asphalts before and after aging: (*A*) A1, (*B*) A2, (*C*) A3, (*D*) A4, and (*E*) A5.

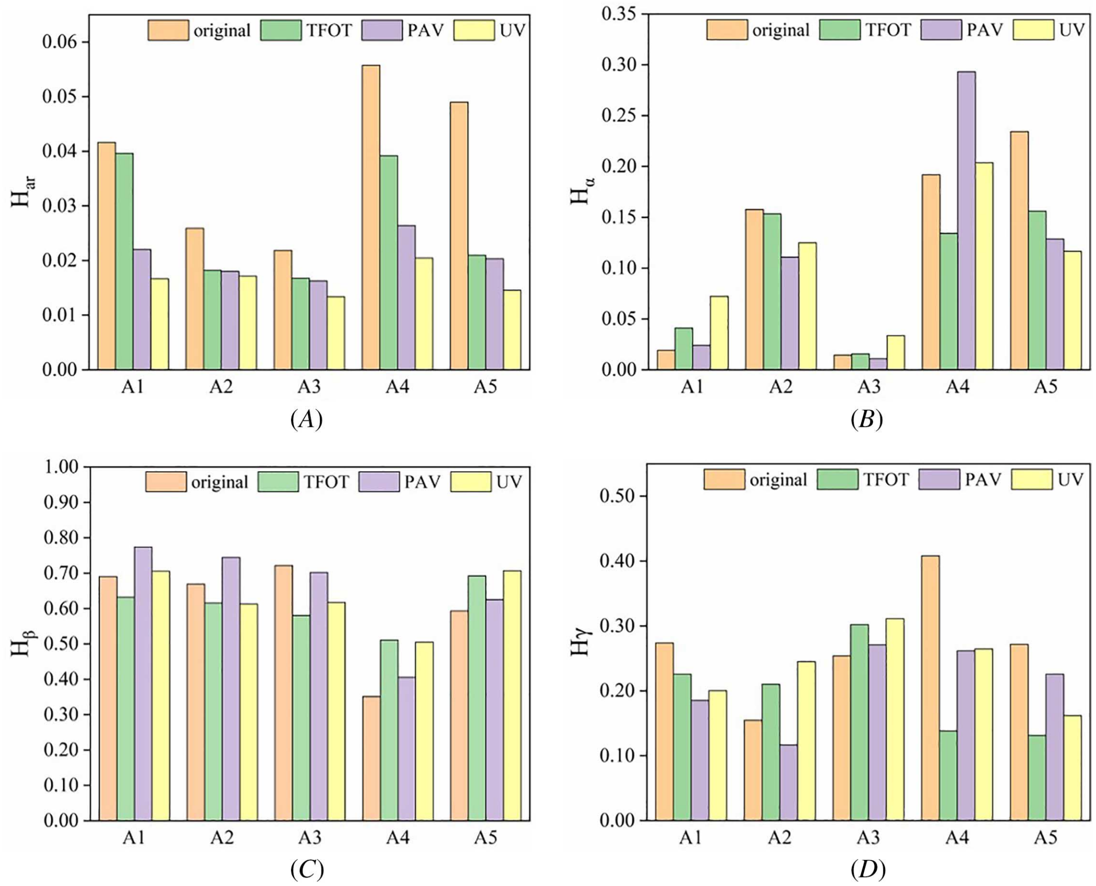


(*A*) (*B*)

(*C*) (*D*)

(*E*)

FIG. 6 Hydrogen atom distribution of all asphalts before and after aging: (*A*) the contents of H_{ar}, (*B*) the contents of H_{α}, (*C*) the contents of H_{β}, and (*D*) the contents of H_{γ}.



(*A*) (*B*)

(*C*) (*D*)

Figure 6*B* and **6*D*** showed the H_{α} and H_{γ} content didn't show a clear trend, and the change of H_{α} content indicated that the asphalt was isomerized during the aging process. In the TFOT aging condition, the H_{α} content of A2, A4, and A5 showed a decreasing trend, which may be because of the higher short-term aging temperature and the aromatization of alkyl-substituted naphthenic rings. The increase of H_{γ} content of A2, A3, and A5 indicated that the side chain breaking reaction occurred after aging. **Figure 6*C*** showed the content of H_{β} changed slightly, ranging from 0 to 0.2.

Comparing the magnitude of variation for distinct hydrogen content, the hydrogen content of A3 before and after aging was relatively smaller than that of other asphalts, indicating that the A3 has a strong antiaging ability, which is consistent with that of FTIR.

Conclusion

This study investigated the impact of aging on the molecular structure of asphalts from different crude oils by elemental analysis, FTIR, and ^{1}H-NMR. The following conclusions can be drawn:

1. Elemental analysis revealed that the H/C of asphalts from different crude oils ranges from 1.347 to 1.602. The content of sulfur, nitrogen, and oxygen varies among different types of asphalts.

2. FTIR analysis indicated that the aromatic index, carbonyl index, and sulfoxide index of the five asphalts increased, while the aliphatic index decreased after aging. The change rate of the carbonyl index of the original asphalt with low H/C was small. Asphalt was more likely to produce the sulfoxide group during the PAV aging process. The aliphatic structure of asphalt decreased more during the UV aging process.
3. ^{1}H-NMR showed that the H_{ar} content decreased after aging. It indicated that the aromatic structure continuously condensed. The asphalt with a low H_{ar} content had a smaller change rate of hydrogen atom content after aging, showing better antiaging performance.
4. The comprehensive analysis of the research results showed that A3 had a strong antiaging ability. The asphalt with lower H/C and H_{ar} content showed better aging resistance.

Future research can proceed from the following aspects: The investigation of the aging resistance of asphalts from different crude oils based on molecular structure and physical and rheological properties, and the relationship between the chemical structure and the physical and rheological properties of asphalt.

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