

MONITORING OF COMPOSITIONAL CHANGES OCCURRING DURING THE OXIDATIVE AGING OF TWO SELECTED ASPHALTS FROM DIFFERENT SOURCES

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Abstract

The aging behavior and sensitivity of two asphalts from different sources (Ural, Russia and Cold Lake, Canada) were studied. The rolling thin film oven test (RTFOT) and pressure aging vessel (PAV) were used to simulate the oxidative aging. Both asphalts were separated into fractions using the ASTM D 4124-01 (Corbett) separation method. The elemental analysis and Fourier transform infrared spectroscopy (FTIR) were used to investigate the chemical composition and structural parameters of both asphalts and their fractions. Elemental analysis showed differences in carbon and sulfur contents and an increase in oxygen content on aging. FTIR revealed that an increase of oxygen was caused mainly by carbonyl and sulfoxide groups. FTIR also showed a higher content of arylalkylketones and a higher content of oxidizable sulfur compounds in fractions of the Ural asphalt.

Key words: asphalt; aging; oxidation; chemical composition

1. Introduction

It is known that the processing of asphalt binder with aggregates, the road construction phase ^[1], and also the ambient conditions during pavement field service (air, water, sun radiation) have significant impacts on the chemical and physical properties of asphalt binder ^[2, 3]. It has also been acknowledged that the chemical properties of asphalt binders and their sensitivity to aging are affected by their chemical composition, which depends on the source of the asphalt ^[4, 5].

Petroleum asphalt used as a binder in road construction reacts slowly with the atmospheric oxygen during its service life ^[2]. Oxidation of asphalt binder is accompanied by its embrittlement, which can lead to various forms of pavement cracking and can ultimately cause pavement failure. Oxygen-containing chemical compounds, initially present in asphalt or formed because of oxygen uptake, are generally highly polar and capable of strong interactions. These interactions are believed to be responsible for the hardening and embrittlement of asphalt pavement ^[6].

A fundamental problem for the determination of asphalt's chemical composition and changes in its chemical composition lies in the tremendous chemical complexity of asphalt. Fortunately, this issue can be solved by the separation of asphalt into fractions that can be more easily characterized ^[7].

Moschopedis and Speight ^[8] have suggested that the elemental composition of asphalts and their fractions can be used as a guide to the changes in composition that take place during air-blowing (oxidation) of the asphalt materials. Oxidation reactions can cause an increase in the content of oxygen or can be responsible for the elimination of sulfur and/or nitrogen atoms ^[9]. Petersen ^[10] also suggested that, besides the oxygen uptake, some elimination of nitrogen and sulfur atoms can occur, and it is possible that eliminated sulfur may, in turn, act as a condensing agent.

Probably the most extensively used method for the determination of compositional changes that take place during the oxidation of asphalt material is Fourier transform infrared spectroscopy (FTIR).

The infrared absorption spectrum between 1600 cm^{-1} and 1900 cm^{-1} is of particular interest, because it contains absorption bands belonging to functional groups, such as carboxylic acids, esters, ketones, or anhydrides [5, 11]. All these compounds contain infrared active carbonyl C=O bonds and are, therefore, used to measure the amount of asphalt aging [5]. Similarly, sulfoxide forms of sulfur, which are formed during the oxidation, can be determined by FTIR, utilizing a very strong band at about 1030 cm^{-1} [12].

The main goal of this paper is to discuss the aging behavior of our selected asphalts and to show how the different origins and chemical compositions of these asphalts can affect their aging sensitivity.

2. EXPERIMENTAL

2.1 Materials

The bitumens used in this study were commercially produced vacuum residues, originating from two different sources (Ural, Russia, Penetration grade 150/200; Cold Lake, Canada, Penetration grade 200/300) and collected from the refineries of SLOVNAFT in Slovakia and Husky Energy in Canada, respectively. Both asphalts were characterized using conventional and Superpave (Superior Performing Asphalt Pavements) tests of physical properties (Table 1). The rolling thin film oven test (RTFOT) [13] and pressurized aging vessel (PAV) [14] were applied to simulate the oxidative aging of these asphalts. RTFOT simulated short-term aging that takes place during the hot mixing of asphalt binder with aggregates and pavement construction, while PAV simulated the long-term aging that the asphalt is subjected to during its service life. Hence, the original samples were used for RTFOT, and the RTFOT aged samples were used for PAV aging simulations.

2.2 Methods

The ASTM D 4124-01 [15] method of separation of asphalts into four fractions (the Corbett method) was used to separate asphalts into asphaltenes, saturates, naphthene aromatics and polar aromatics, and to observe changes in their chemical composition during the aging process. The principle of this separation method is based on the different solubility of chemical compounds in solvents with varying polarity. In the first step, n-heptane insoluble asphaltenes were separated from n-heptane soluble malthenes. In the next step, the remaining malthene fraction was adsorbed on activated F-20 alumina and further fractionated into the saturate, naphthene aromatic and polar aromatic fractions in a glass chromatographic column. Eluted fractions were recovered by solvent removal until the constant weight was achieved.

Table 1. Conventional and Superpave characterizations of the selected Ural (Russia) and Cold Lake (Canada) asphalts.

Asphalt	Cold Lake	Ural
Standard Tests		
Penetration at 25°C, [dmm] (100g/5s)	260	186
Softening point, [°C]	37	39
SHRP Tests		
Original Binder Properties		
Viscosity at 135°C, [mPa.s]	199	184
Dynamic Shear ($G^*/\sin\delta$), (Min. 1.0 kPa), [kPa]	1.02	1.01
Temperature, [°C]	53	53
RTFOT (T240)		
RTFOT Mass Loss, [%]	-0.844	+0.017
Dynamic Shear ($G^*/\sin\delta$), (Min. 2.20 kPa), [kPa]	2.20	2.27
Temperature, [°C]	54	52
Pressure Aging Vessel Residue		
PAV Aging Temperature, [°C]	90	90
Dynamic Shear [$G^*(\sin\delta)$], (Max. 5000 kPa), [kPa]	3490	3590
Temperature, [°C]	13	19
Creep Stiffness (S-max. 300 Mpa) @ 60 s	278	257
(M value – min. 0.300) @ 60 s	0.320	0.303
Temperature, [°C]	-26	-18
Actual Grading	PG53-36	PG52-28
High Temperature/Low Temperature Spread	89	80
Superpave M 320 Grading	PG52-34	PG52-28

Elemental analysis of the asphalts and their fractions was performed on a gas chromatography unit, Carlo Erba 1106. The contents of carbon, hydrogen and nitrogen were determined by combustion of the sample in oxygen; and, the resulting carbon dioxide, water and nitrogen were measured by thermal conductivity and compared directly with known acetanilide and nitro aniline standards. Oxygen was analyzed in a similar way, but carbon monoxide was formed and measured by thermal conductivity. The sulfur content was determined by titration. After combustion, absorption and pH adjustment, the resulting solution was titrated with standardized barium per chlorate by a volumetric method, using thorin as the indicator.

Infrared spectra of asphalts and their fractions were recorded from their films laid on sodium chloride (NaCl) plates, using a Nicolet Nexus 670 spectrometer. The films were deposited from tetrahydrofuran solutions by evaporating the solvent. Spectra were recorded with 64 scans and 4 cm⁻¹ resolution and were measured in a range of wavenumbers from 4000 to 625 cm⁻¹. Because of the different thicknesses of the sample films on the NaCl plates, the spectra were normalized, in order to be compared [16]. Sample preparation and spectra recordings were done three times for each sample. The reported results represent the average of these three tests. The structural indices were calculated from the band areas [17], which were measured from valley to valley (Figure 1), because several vibrations of the same type are taken into account (carbonyl index vibrations of carboxylic acids, esters, anhydrides or ketones). The calculated structural indices were subsequently used to determine and compare chemical composition and changes in chemical composition of the Cold Lake and Ural asphalts and their fractions on aging. These indices are defined as follows [18]:

Carbonyl index (C=O): $A_{1700}/\Sigma A$

Sulfoxide index (S=O): $A_{1030}/\Sigma A$

Aromaticity index: $A_{1600}/\Sigma A$

The sum of the area ΣA represents: $A_{1700} + A_{1600} + A_{1460} + A_{1376} + A_{1030} + A_{864} + A_{814} + A_{743} + A_{724} + A_{(2953, 2923, 2862)}$

Fourier self-deconvolution was used for qualitative analysis, thus identifying the presence of various types of carbonyl compounds by resolving overlapping peaks in the carbonyl region. The Gauss-Lorentz function was used for semi-quantitative analysis to separate overlapping peaks in the carbonyl region between 1500 -1800 cm⁻¹, and to determine and compare areas of individual bands using a band fitting program (Figure 2).

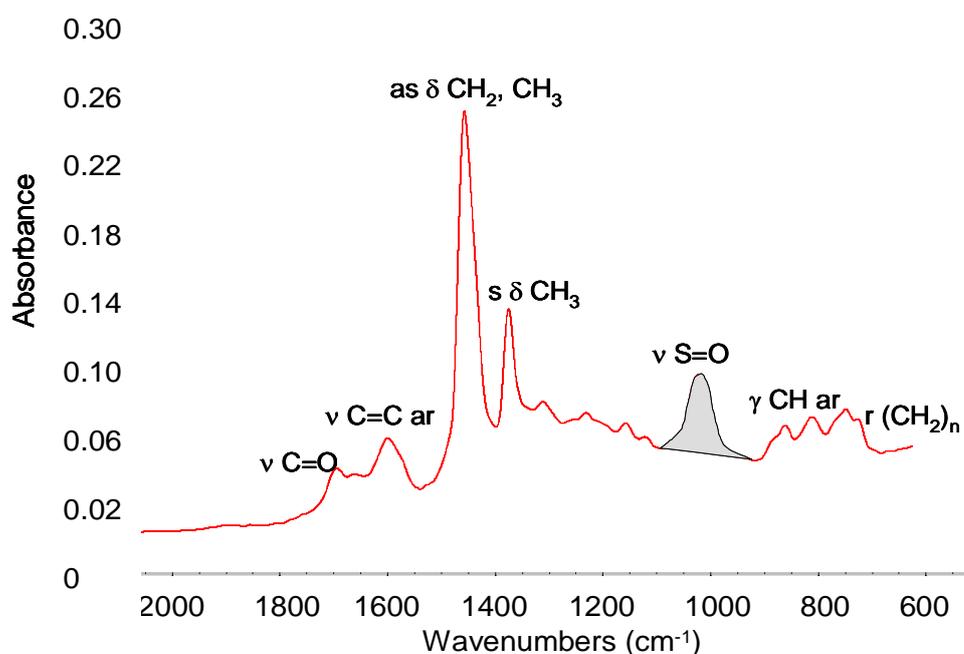


Figure 1. Visualization of sulfoxide band area (1030 cm⁻¹) integration (valley to valley) [17].

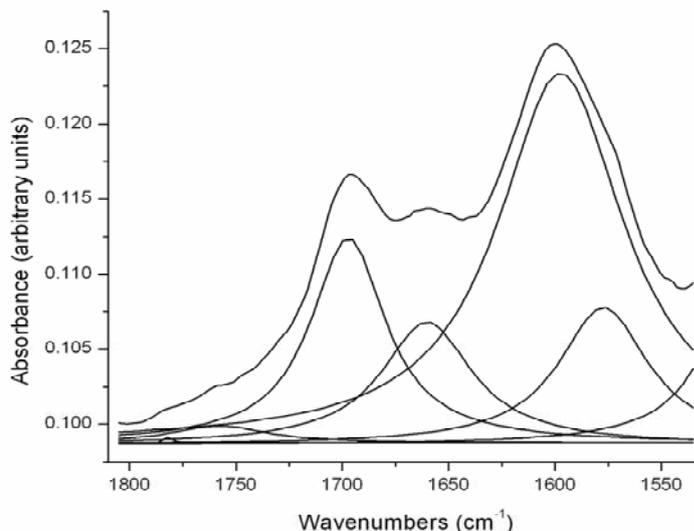


Figure 2. Band fitted infrared spectrum of asphalt between 1500 -1800 cm^{-1} .

3. Results and discussion

The chemical composition of the Cold Lake and Ural asphalts determined by the Corbett separation method is given in Table 2. The separation confirmed that transformation of naphthene aromatics into polar aromatics and polar aromatics into asphaltenes took place on aging [19]. Fractional composition further revealed that the Russian asphalt was more sensitive to aging; and, changes in its composition were more significant.

Table 2. Fractional composition of the original and aged Cold Lake and Ural asphalts.

Asphalt	Fraction, weight %			
	Saturates	Naphthene aromatics	Polar aromatics	Asphaltenes
Ural original	6.6	48.5	37.2	7.8
Ural RTFOT	6.2	48.1	36.8	9.4
Ural PAV	6.4	41.5	40.6	11.8
Cold Lake original	13.6	41.6	30.6	14.4
Cold Lake RTFOT	13.3	40.2	29.8	16.6
Cold Lake PAV	13.4	36.8	30.7	19.6

The elemental composition data presented are the means of the three determinations and are shown in Tables 3 and 4. Results of the elemental analysis showed slightly higher contents of carbon and nitrogen in the Ural asphalt and comparable contents of hydrogen in both asphalts.

Table 3. Elemental compositions of the original and aged Canadian (Cold Lake) and Russian (Ural) asphalts.

Asphalt	Elemental composition wt. %					
	C	H	N	O	S	H/C
Cold Lake original	83.17	10.28	0.45	1.33	4.77	1.47
Cold Lake RTFOT	83.28	9.99	0.47	1.41	4.85	1.43
Cold Lake PAV	82.97	10.02	0.46	1.94	4.61	1.44
Ural original	85.20	10.30	0.58	1.25	2.67	1.44
Ural RTFOT	84.91	10.35	0.63	1.42	2.69	1.45
Ural PAV	84.80	10.20	0.61	1.76	2.63	1.43

The most significant difference between the elemental compositions of these two asphalts was in the content of sulfur (Table 3). The sulfur content in the Cold Lake asphalt was almost twice as high as

that in the Ural asphalt. The contents of oxygen were comparable and followed a reasonable increase on aging, especially after PAV, indicating the possible creation of carbonyl (C=O) and sulfoxide (S=O) groups. No sulfur or nitrogen elimination, as mentioned by Moschopedis [9] and Petersen [10], was observed.

Table 4. Elemental compositions of the original and aged Cold Lake (Canada) and Ural (Russia) asphalt fractions.

Sample	Elemental composition wt. %					
	C	H	N	O	S	H/C
Cold Lake original saturates	86.22	12.83	0.30	0.95	0.30	1.77
Cold Lake RTFOT saturates	86.50	12.43	0.30	1.07	0.30	1.71
Cold Lake PAV saturates	85.57	13.51	0.30	0.92	0.30	1.88
Ural original saturates	85.71	13.18	0.30	1.11	0.30	1.83
Ural RTFOT saturates	85.21	13.64	0.30	1.15	0.30	1.90
Ural PAV saturates	85.36	13.48	0.30	1.16	0.30	1.88
Cold Lake original naphthene aromatics	84.92	10.35	0.30	1.03	3.70	1.45
Cold Lake RTFOT naphthene aromatics	84.86	10.72	0.30	1.02	3.40	1.50
Cold Lake PAV naphthene aromatics	85.21	10.74	0.30	1.02	3.03	1.50
Ural original naphthene aromatics	85.40	11.23	0.30	1.08	2.29	1.56
Ural RTFOT naphthene aromatics	85.78	10.83	0.30	1.07	2.32	1.50
Ural PAV naphthene aromatics	85.94	10.92	0.30	1.06	2.08	1.51
Cold Lake original polar aromatics	81.67	9.31	0.78	1.90	6.34	1.36
Cold Lake RTFOT polar aromatics	81.96	9.65	0.60	1.89	5.90	1.40
Cold Lake PAV polar aromatics	82.21	9.05	0.62	2.39	5.73	1.31
Ural original polar aromatics	83.91	9.82	1.06	1.94	3.27	1.39
Ural RTFOT polar aromatics	83.86	9.79	0.93	2.20	3.22	1.39
Ural PAV polar aromatics	83.72	9.83	0.84	2.55	3.06	1.40
Cold Lake original Asphaltenes	81.42	7.77	1.09	1.70	8.02	1.13
Cold Lake RTFOT Asphaltenes	81.37	7.68	0.92	2.22	7.81	1.12
Cold Lake PAV Asphaltenes	80.67	7.30	1.02	3.18	7.83	1.08
Ural original Asphaltenes	86.10	7.28	1.48	1.56	3.58	1.01
Ural RTFOT Asphaltenes	85.86	7.10	1.43	2.23	3.38	0.98
Ural PAV Asphaltenes	84.39	7.40	1.35	3.25	3.61	1.04

The elemental analysis of asphalt fractions provided valuable information about chemical changes taking place in both asphalts on aging (Table 4). In general, the contents of carbon and hydrogen decreased with the increasing molecular weight of the fractions; while contrarily, the contents of the heteroatoms (sulfur, nitrogen, oxygen) increased. All these trends are reasonable; since, with increasing molecular weight, the fractions become more condensed and contain more heteroatoms [5]. As for the fractions of saturates, no evidence was observed of the development of any functional groups on aging. It seems that the fractions of naphthene aromatics also did not change much on aging, because no increase in oxygen content was observed (Table 4). The most probable explanation of this phenomenon may be that a certain portion of naphthene aromatics turned into polar aromatics on aging, due to oxygen uptake and an increase in polarity. The fractions of polar aromatics and asphaltenes confirmed the expected sensitivity towards oxidation reactions and showed a significant increase in oxygen content, especially after PAV aging (Table 4).

FTIR spectra of the asphalt fractions further revealed that for an increase in oxygen content during the aging were responsible mostly two types of compounds – compounds with absorption spectrum in the carbonyl (C=O, $\sim 1700\text{ cm}^{-1}$) and sulfoxide (S=O, $\sim 1030\text{ cm}^{-1}$) regions [20] – see Figures 3 and 4.

Because no important changes in the carbonyl and sulfoxide areas of the saturate and naphthene aromatic fractions were observed, the Fourier self-deconvolution and Gauss-Lorentz separation with peak area determination are shown only on aging-sensitive fractions of the polar aromatics and asphaltenes (Figures 2 and 5).

Fourier self-deconvolution, which was used to identify different types of compounds responsible for the increase in oxygen content on aging, revealed the presence of similar types of functional groups in the fractions of both asphalts. Table 5 shows infrared band assignments of compounds typically present in the carbonyl region.

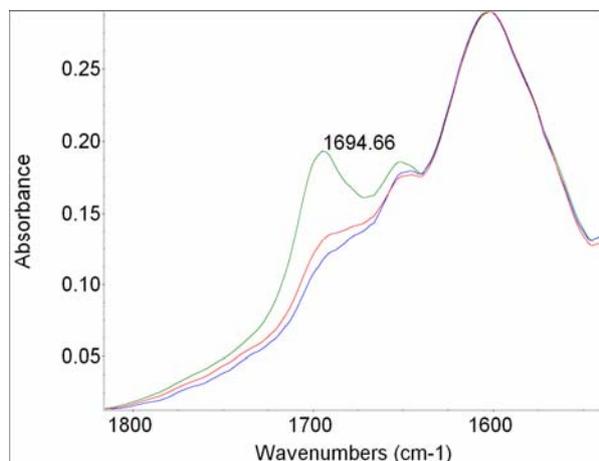


Figure 3. Infrared spectra of the Ural asphalt at various aging stages (C=O region).

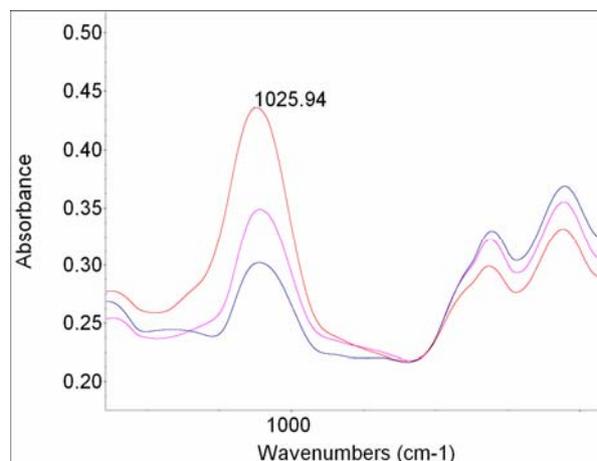


Figure 4. Infrared spectra of the Cold Lake asphalt at various aging stages (S=O region).

Table 5. Infrared band assignments of compounds typically present in the carbonyl region ^[20].

Compound	Frequency (cm-1)
carboxylic acid	1730
diarylketone or quinone structure	1660
arylalkylketone	1695
ester	1760, 1740
ester or anhydride	1780

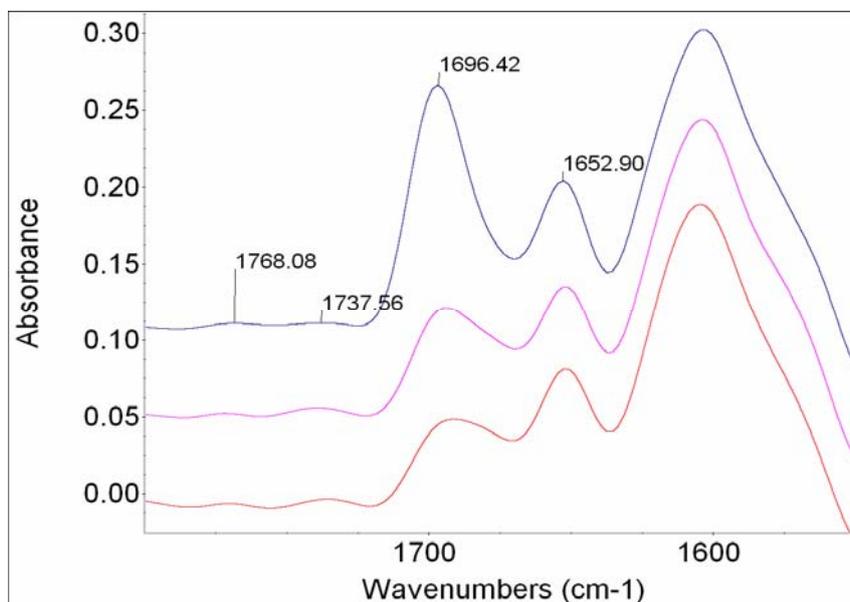


Figure 5. FTIR spectra of the Ural (Russia) polar aromatic fractions after Fourier self-deconvolution.

The FTIR spectra of the asphalt fractions revealed a strong presence of ketone structures at 1655 cm^{-1} (diarylketone or quinone structures) and at 1695 cm^{-1} (arylalkylketones) ^[20]. Furthermore, although very weak, the presence of carboxylic acids (together with broad band at 3500-3200 cm^{-1}) or esters at 1730-1740 cm^{-1} (Ar-CO-O-H, Ar-CO-O-R) and esters or anhydrides at 1770 cm^{-1} (R-CO-O-Ar) were also observed ^[20]. Figure 5 shows Fourier self-deconvolution of the spectra of the Ural polar

aromatic fraction at different aging stages. The growth of arylalkylketones (1695 cm^{-1}) on aging was especially extensive, while no significant changes in other types of the carbonyl functional groups were observed.

With the help of the Gauss-Lorentz function, which was used to resolve overlapping and interfering absorption bands in carbonyl area and to determine areas of individual peaks (Figure 2), structural parameters, such as the carbonyl and sulfoxide indices, were calculated^[18] (Table 6).

Table 6. Carbonyl and sulfoxide indices of the polar aromatic and asphaltene fractions of the Cold Lake and Ural asphalts.

Fraction	Carbonyl index %	Sulfoxide index %
Cold Lake original polar aromatics	0.3	0.9
Cold Lake RTFOT polar aromatics	0.4	1.8
Cold Lake PAV polar aromatics	0.9	3.5
Ural original polar aromatics	0.3	0.8
Ural RTFOT polar aromatics	0.4	1.6
Ural PAV polar aromatics	1.2	3.6
Cold Lake original asphaltenes	0.2	0.7
Cold Lake RTFOT asphaltenes	0.3	0.9
Cold Lake PAV asphaltenes	1.1	2.9
Ural original asphaltenes	0.2	0.6
Ural RTFOT asphaltenes	0.3	0.8
Ural PAV asphaltenes	1.3	1.7

The fractions of polar aromatics and asphaltenes, sensitive to oxidative aging, revealed an increase in the carbonyl index from the original asphalt samples to the RTFOT and PAV aged samples. Data also revealed that PAV aging, which simulated the long-term aging that takes place during the service life of the asphalt pavement, caused a very significant increase in the content of carbonyl functional groups. The fractions of the Ural asphalt were slightly more sensitive towards oxidation, as is shown in Table 6 (the carbonyl index). As was previously shown by Fourier self-deconvolution (Figure 5), the peak centered at 1695 cm^{-1} belonging to arylalkylketones was mainly responsible for this increase in the carbonyl index. This fact begs the question – does the aromatic character of our asphalt fractions play a role in asphalt aging and the formation of arylalkylketones? The aromaticity index, calculated for the fractions of our asphalts, revealed that the Ural asphalt fractions with higher values of carbonyl indices also had higher aromaticities (see Figure 6). Further investigation of these fractions did not show any important changes in their aromaticities on aging.

Aromaticity itself, however, is not sufficient to correctly assess the tendency of asphalt to form oxygen-containing aromatic compounds. It is well known that the aromatic ring is very resistant to oxidation^[21]. However, carbon atoms directly adjacent to the aromatic ring (benzylic carbons) containing at least one hydrogen atom are readily oxidizable, and the oxidation of benzylic carbon containing molecules can lead to formation of ketones or to further carboxylic acids^[22].

Because no significant change was observed in the carboxylic and anhydride absorption bands of our samples, it is possible to assume that oxidation of alkyl aromatics into arylalkylketones took place on aging. Therefore, it is also possible to conclude that the Ural asphalt with a higher content of carbon atoms (Table 3) and greater aromatic character (a higher content of benzylic carbons, due to a higher number of aromatic rings with side alkyl chains, Figure 6) probably had a higher number of alkyl aromatics with oxidizable benzylic carbons. Thus, the carbonyl indices of the fractions of this asphalt after PAV were higher than the carbonyl indices of fractions of the Canadian Cold Lake asphalt.

The calculated sulfoxide indices revealed similar behavior for the asphalt fractions. The fractions of polar aromatics were the most sensitive to oxidative aging, and their values of sulfoxide indices were the highest among all fractions. Again, especially after PAV aging, there was a sharp increase in the sulfoxide index observed.

It is worth noting that the sulfoxide indices of both the Ural and Cold Lake polar aromatic fractions were growing at almost the same rate. This is very interesting, because the content of sulfur in the Cold Lake polar aromatic fractions (about 6%) was almost twice as high as that in the polar aromatics

of the Ural asphalt (about 3%). This may indicate that the significant part of the sulfur in the Ural polar aromatics is present in the form of oxidizable compounds. According to Herrington [23], the aliphatic sulfur forms (sulfides, disulfides, etc.) are sensitive to oxidation and can be oxidized to sulfoxides. This also indicates that the important part of the sulfur present in the Canadian Cold Lake asphalt may be present in the form of nonsensitive aromatic sulfides or thiophenic compounds.

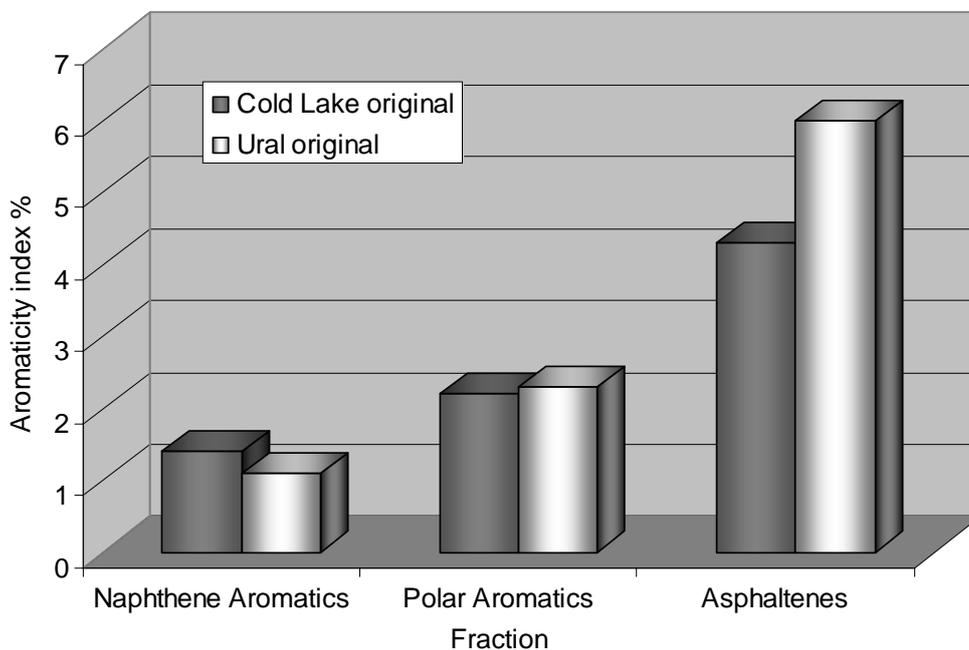


Figure 6. Aromaticity indices of fractions of the Cold Lake and Ural asphalts.

Kasrai *et al.* [24], using X-ray absorption fine structure spectroscopy in his study of sulfur types present in bitumens and asphaltenes, showed that the most dominant type of sulfur were thiophenes. Petersen and Martin [25, 26], while oxidizing asphalts at 130°C and 60°C (300 psi O₂), observed that sulfoxide concentration, after an initial increase, reached a constant value. They provided two possible explanations: further oxidation of sulfoxides to sulfones, or sulfoxide decomposition. If the sulfones are being formed, a rise of the characteristic IR absorption bands between 1360-1290 cm⁻¹ and 1170-1120 cm⁻¹ should then occur [27]. In the case of our Ural and Cold Lake asphalts, the investigation of the bands absorbing in these areas did not show any important changes in peak intensities on aging which would indicate the creation of sulfone groups. Similarly, the elemental analysis did not show any important changes in the content of sulfur on aging which would indicate sulfoxide decomposition.

The sulfoxide indices of asphaltenes were lower than the S=O indices of polar aromatics. This is understandable, because asphaltenes are the fractions with the highest molecular weights, and sulfur is usually present in the form of non-oxidizable thiophenic compounds. Furthermore, after being aged, a part of the polar aromatic fraction becomes asphaltenes. It is, therefore, probable that a majority of the oxidizable sulfur was already oxidized.

It is worth highlighting an interesting difference in the behavior of the polar aromatic and asphaltene fractions of both asphalts on aging. In polar aromatics, despite the different sulfur content, the values of the sulfoxide indices in both asphalts were similar; however, in asphaltenes, the different sulfur content resulted in different sulfoxide indices, especially after PAV (~7.9% of sulfur in Cold Lake asphaltenes; ~3.6% of sulfur in Ural asphaltenes). This fact indicates more significant differences in the types of sulfur present in the polar aromatic and asphaltene fractions of the Ural asphalt. Aliphatic, oxidizable sulfur compounds probably constitute the important portion of the polar aromatics of the Ural asphalt, while in its fraction of asphaltenes, thiophenic types of sulfur compounds are probably dominant.

4. CONCLUSIONS

Our investigation of two selected asphalts from different sources confirmed the dependence of an asphalt's chemical composition on its origin and also showed the relationship between the chemical composition of the asphalt material and its sensitivity to aging. The Corbett separation method showed

how significantly the Ural and Cold Lake asphalts differed in their fractional composition. The fractionation showed that the Russian Ural asphalt was more sensitive to aging and that changes in its chemical composition were more significant than changes in the composition of the Cold Lake asphalt. The elemental analysis also revealed important differences in the elemental composition of these asphalts, especially in the contents of carbon and sulfur.

The laboratory simulation of the hot mixing of the asphalt with aggregates (RTFOT) and the aging of the asphalt during its service life (PAV) showed how significant changes in asphalt can occur on aging. FTIR identified the gradual growth of bands absorbing in the carbonyl ($\sim 1700\text{ cm}^{-1}$) and sulfoxide ($\sim 1030\text{ cm}^{-1}$) areas. The resolution of overlapping peaks, with the help of Fourier self-deconvolution, revealed the presence of different types of compounds with infrared active C=O functional groups (carboxylic acids, esters, anhydrides, ketones). The arylalkylketones (1695 cm^{-1}) were the most significantly growing carbonyl compound.

The calculation of the carbonyl and sulfoxide indices using the Gauss-Lorentz function to determine band areas showed the higher sensitivity of the Ural asphalt to aging (the carbonyl index). Furthermore, the calculation of the sulfoxide index revealed possible differences in the types of sulfur compounds in our selected asphalts. The polar aromatic fraction of the Ural asphalt was probably rich in oxidizable aliphatic sulfur compounds (lower sulfur content but similar sulfoxide index), while the fractions of asphaltenes of both asphalts probably contained mainly non-oxidizable sulfur compounds of the thiophenic type.

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