

ARABIAN ASPHALTS-CHEMISTRY AND RHEOLOGY

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INTRODUCTION

The entire roadway network in the kingdom is built using flexible pavements due to the availability of relatively low cost asphalt binders. Despite the enforcement of strict specification of materials, the other factors such as heavy loads and high tire pressure etc. have resulted in premature pavement failure in the form of rutting, cracking and deformation in some parts of the countries. This type of damage if not controlled effectively could cost millions of dollars in road repairs. This paper presents a study in which the virgin Arabian asphalts were analyzed for their chemical and rheological properties and their results were compared with artificially aged asphalts.

The asphalts examined in this study were collected from the four Arabian refineries namely Ras Tanura (RT), Saudi Arabia, Riyadh (RY), Saudi Arabia, Kuwait (KW), and Bahrain (BH). A detailed analysis and discussion of the test results are presented here.

Laboratory Aging of Asphalt

Temperature has a great influence on the flow, brittleness, and consistency of asphalt. Since asphalt is composed of enormously large hydrocarbons, the temperature gradually changes its physical and chemical composition from semi-solid to fluid. The aging or oxidation of asphalt is one of the important factors most commonly used for the characterization of asphalt properties (1). There are two types of laboratory methods used for the aging of Arabian asphalts. The first is the short term aging due to the plant mixing or the laydown process. For this method, the Rolling Thin-Film Oven Test (RTFOT), ASTM D-2872 was used which indicate approximate changes in the properties of asphalt during conventional hot mixing at about 150°C. The second type is long term aging due to in-situ field aging. This was simulated by means of a Pressurized Aging Vessel Test (PAV) which uses residue from the RTFO test method. The residue of this test is used to estimate the physical and chemical properties of an asphalt after five to ten years of aging in the field.

Rheological Properties of Asphalt

Twenty samples of virgin asphalts from the four refineries were tested for their rheological properties. Table I shows a summary of average consistency tests results for the four refinery asphalt samples. Penetration @ 25°C, viscosity, softening point, and ductility are the most common tests in use by refineries to characterize the asphalt cement consistency. The sample from Bahrain refinery (BH) met the 40/50 penetration grade, Ras Tanura refinery sample (RT) met the 60/70 penetration grade, while the rest of the samples did not meet any penetration grades. Softening point of all refinery samples ranged within 49.5±1. The rotational viscosity @ 135°C ranged from 465 to 530 Cp. The test results in Table I also shows that laboratory aging (RTFOT) causes a decrease in penetration, and an increase in absolute viscosity of all samples.

The measured physical and consistency properties were used to calculate temperature susceptibility indices such as: penetration ratio, penetration index, penetration viscosity number (PVN) based on viscosity @ 60°C and 135°C, and viscosity-temperature susceptibility (VTS). A high PVN and low VTS indicate minimum susceptibility. Asphalts with high temperature susceptibility may contribute to rutting at high temperature and cracking at low temperatures. The following generalized observations are drawn from the test results (Table II).

The penetration ratio (PR) of all samples ranged from 40.71 to 53.97. Low PR indicates large temperature susceptibility. The retained penetration (PR) at 25°C decreases from RT>BH>RY>KW, thus indicating low heat hardening for RT sample and high heat hardening for KW samples.

Elemental Analysis of Asphalts

The physical nature and the behaviour of asphalts are determined by the hydrocarbons, heteroatoms and metal content composing them. Weight percent of carbon, hydrogen, nitrogen, oxygen, sulfur and their atomic ratios of the four Arabian fresh asphalts are shown in Table-III. The ratios classify various group types and provides basic information about chemical composition of asphalt which in turn might be related to the source and process technique.

In the samples under examination the H/C ratio was found to be highest of 1.46 in RT asphalts followed by 1.44 (KW), and then 1.43 for RY and BH. Higher H/C ratios indicate more aliphatic character and lower ratios indicates more aromatic character. So, the RT asphalt is most paraffinic in nature while RY and BH asphalts are more aromatic in nature.

The heteroatom contents of asphalt are of great significance. The S/C ratio was found to be highest in KW and lowest in RT asphalt, while RY and BH had intermediate values. These ratios clearly indicate that the asphalts in this study have different origin and chemistry. Similarly, O/C, and N/C ratios were again found to be at a maximum in KW asphalt. These values again emphasize that the KW asphalt has a different chemical composition and therefore genesis from the other Arabian asphalts. The heteroatom contents vary more than the hydrogen-carbon ratios in these asphalts of different sources.

Weight Percent of Generic Fractions

Asphalt composition is largely dependent upon the source and origin of the crude oil from which it is derived. Generally, composition is based upon the quantitative determination of the four generic fractions, i.e. asphaltenes, polar aromatics, naphthene aromatic, and saturates, present in all asphalt (2). The composition of asphalt from Ras Tanura refinery is given in Table IV. It was observed that each of these fractions of Arabian asphalt were different from one another in color, weight percent, density and aromatic carbon contents. It was also found that saturates were colorless, naphthene aromatics were yellow to red in color, while polar aromatics was black and asphaltene brown to black in color.

Saturates and naphthene aromatics were liquids at room temperature, while polar aromatics were semi-solids, and asphaltenes were solid in nature. Weight percent of all four generic fractions in each fresh and aged asphalt was found to be quite consistent. Naphthene aromatics constituted the highest weight percent followed by polar aromatics, then asphaltenes and then saturates.

It was concluded that the naphthene aromatics converted in part to polar aromatics and which later turned to asphaltenes on RTFO and PAV aging tests. It was also noted that there was a slight increase in the saturates following oxidation but the results were not consistent and the differences were very small. Changes in Arabian asphalt composition following RTFO and PAV aging tests may not be identical and consistent from the chemistry point of view but directionally were similar. There are several possible reactions and mechanisms following the short-term and long-term aging of Arabian asphalts. Some of these reactions might be condensation with ester formation, polymerization or isomerization, dehydrogenation, aromatization, and dealkylation. The extent of these reactions varies in all four Arabian asphalts.

HP-GPC Analysis of Asphalt

The HP-GPC fractions, using eight equal elution times fraction method (3), for the neat and aged asphalts from the four Gulf refineries are tabulated in Table V. The results show that aging causes a significant increase in the LMS region (fraction 1 to 4) and a decrease in the middle (MMS), and low molecular size (LMS) regions for all samples.

The HP-GPC profiles for the neat samples from the four sources are drawn on the same graph as shown in Figure 1. It is observed that samples from each source carry some shape characteristics which differentiate them from samples from other sources. Also, it can be noticed from this figure that RT and RY samples had more LMS fraction than BH and KW samples. In general, the HP-GPC analysis of the neat and aged samples from the four refineries led to the following conclusions:

- (1) The HP-GPC method of analysis is effective in detecting the asphalt source, asphalt production method and effect of aging and effect of asphalt modification on the molecular size distribution.
- (2) There is an increase in the amount of large molecular size fractions as a result of aging.
- (3) Transformation of molecular size seems to be the reason behind the change in physical properties which occur due to aging. The increase in the amount of LMS leads to decrease in the penetration value and increase in the viscosity of the asphalts.

Infrared Spectroscopy of Generic Fractions

IR spectroscopy was used to study the distribution of functional group types present in the asphaltene, polar aromatics, naphthene aromatics, and saturates of all four Arabian asphalts. IR spectroscopy proved to be a very useful technique in analyzing structural changes in all generic fractions following RTFO and PAV tests of Arabian asphalts. The most prominent IR vibrations of particular interest were those for C-H, C=O, and S=O modes of vibrations and the area of the peaks were determined using the baseline method.

Some parameters calculated from peak areas of selected IR bands allowed for a very useful comparison of the spectra of fresh and aged samples. The ratios in an equation to determine weight percent of oxygen in C=O types and sulfur in S=O types has been used (4).

¹³C Nuclear Magnetic Resonance Spectroscopy of Asphaltenes

Nuclear magnetic resonance (NMR) spectroscopy with proton (¹H) and carbon-13 (¹³C) has proved very useful in following the short term and long term aging processes of the Arabian asphalts at the centre of this study. Structural characteristics are important in determining durability and rheological properties of asphalt. The spectra obtained before and after aging indicate both structural similarities and differences in the generic fractions examined. The narrow range of chemical shifts in ¹H NMR poses serious limitations on the quantitative estimation of hydrogens. In contrast, ¹³C NMR offers a direct observation of the basic carbon skeleton with signals of good resolution (5). The combination of ¹³C and ¹H NMR spectroscopy was used in assessing the average molecular composition of asphaltenes. Only ¹H NMR spectroscopy was used for the analysis of polar aromatics, naphthene aromatics, and saturates fraction of all four Arabian asphalts.

Figure-2 illustrates the percent carbon distribution of RT asphaltenes obtained by ¹³C NMR spectra. The aromatic carbon contents (C_{ar}) first decreased from RT-F to RT-R1, then increased in RT-R4, then again decreased in RT-P1, and finally increased in RT-P4 following the aging process. This trend clearly shows that there were no consistent aromatization and dehydrogenation of asphaltenes but isomerization of saturated carbons (C_{sat}) may be responsible for this type of distribution.

CONCLUSIONS

The chemical characteristics such as class types, molecular size distribution, IR and NMR spectroscopic characterization of asphalt are more effective than the conventional presently used physical tests for predicting performance behavior of asphalts. There is an increase in the amount of asphaltenes and polar aromatics and decrease in the neutral fraction due to aging of asphalt.

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Table III**ELEMENTAL ANALYSIS (wt %) OF ARABIAN FRESH ASPHALTS**

Sample	C	H	S	N	O	H/C	O/C (x10 ⁻³)	S/C (x10 ⁻²)	N/C (x10 ⁻³)
RT - F	84.66	10.41	4.58	0.39	Nil	1.46	Nil	2.03	3.96
KW - F	82.24	9.97	6.48	0.46	0.85	1.44	7.76	2.95	4.81
RY - F	84.25	10.14	4.99	0.41	0.21	1.43	1.87	2.22	4.19
BH - F	84.40	10.11	4.67	0.38	0.44	1.43	3.91	2.07	3.87

Table IV**FRACTIONS OF MALTENES (wt %) OF RAS TANURA (RT) ASPHALT**

Sample	Asphaltenes	Saturates	Naphthene Aromatics	Polar Aromatics	Total (%)	Gaestel Index
RT - F	18.72	12.61	43.70	23.73	98.76	0.46
RT - R1	21.17	13.03	40.56	25.17	99.93	0.52
RT - R4	24.35	13.21	35.15	26.11	98.82	0.61
RT - P1	25.32	13.80	31.42	29.27	99.81	0.64
RT - P4	28.16	13.62	27.05	31.20	100.03	0.72

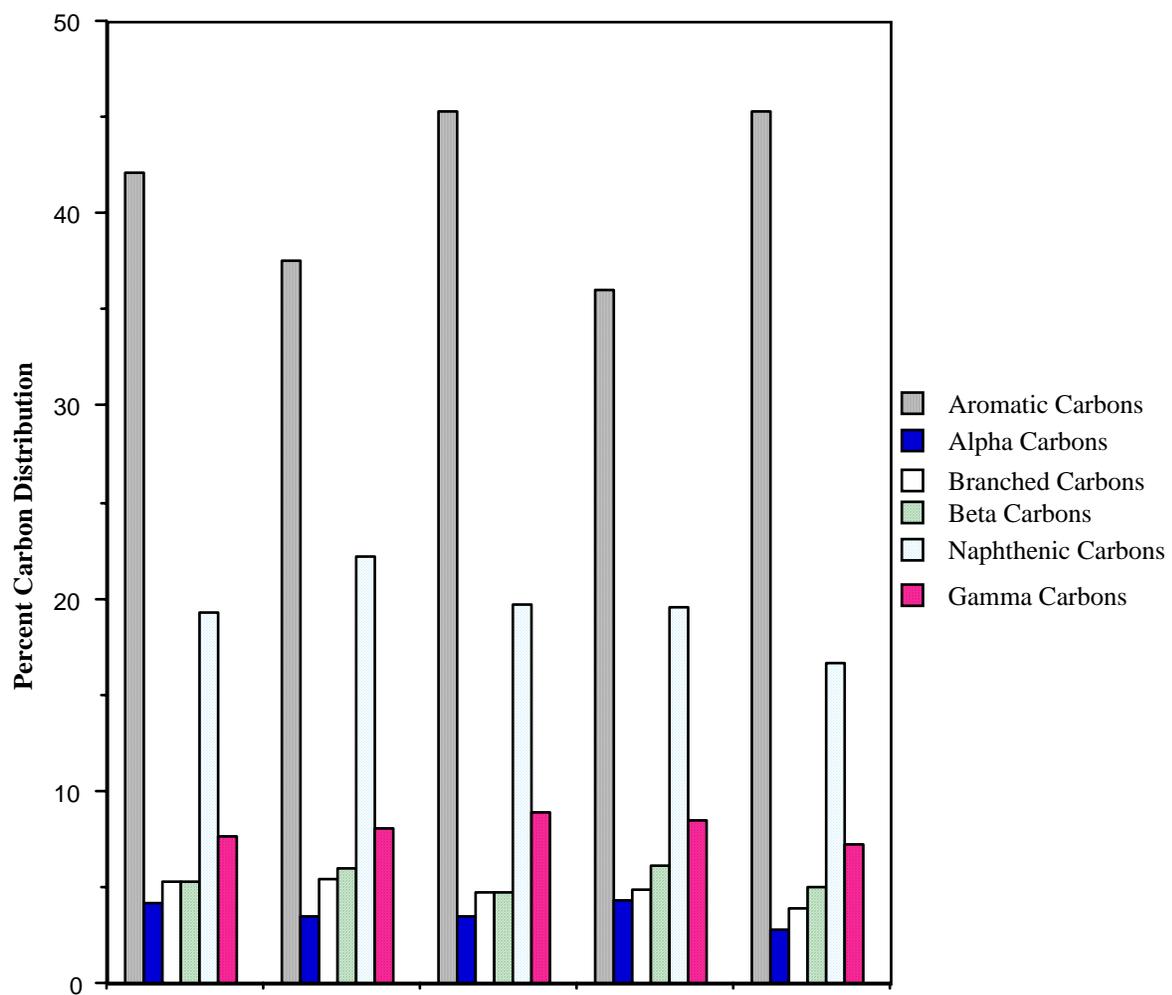


Figure 2: Percent carbon distributions obtained by ^{13}C NMR in RT asphaltenes