Fractional Chemical Composition of Asphalt as a Function of Its Durability

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Abstract

In order to get better understanding of asphalt pavement performance, asphalt from five Iraqi refineries (Qayarah, Nassiriyah, Baiji, Samawah and Daurah) were analyzed into five chemical fractions including asphaltenes, polar compounds, first acidaffins, second acidaffins and saturated hydrocarbons where the last four fractions called maltenes.

Polar compounds /saturated hydrocarbons ratio (PC/S) and the ratio of the reactive to the un-reactive components of the maltenes fraction (durability rating) parameters were determined. The study showed that Baiji asphalt has the best durability over other asphalts, while Qayarah asphalt is considered to have the least durability grade. These results confirm the correlation of the chemical composition of asphalt as a function of its durability.

Introduction

Asphalt, is a sticky, black and highly viscous liquid or semi-solid that is present in most crude petroleums and in some natural deposits termed asphaltum. It is most commonly modeled as a colloid with asphaltenes as the dispersed phase and maltenes (the chemical fractions of asphalt material except asphaltenes) as the continuous phase [1].

Asphalts lose their plasticity and therefore harden and crack or crumble when they lose their more volatile lower molecule weight constituents or when these constituents are oxidized; this process is known as aging. Moisture from rain and other sources can also invade and damage asphalts particularly aged or oxidized asphalts because they have a large number of polar constituents to attract water molecules [2].

Asphalts which are used in the field of construction pavements are specified by using the penetration grading system .The (40-50) penetration grade asphalts that produced from the various refineries in Iraq are most widely used in paving the roads despite Dourah refinery produces other types of asphalts in the grades (40-100).Viscosity may also be considered as an accepted system. Table (1) shows some physical properties of original grades of asphalt and asphalt after aging according to ASTM (D1754) [3].

To obtain a proper idea of asphalt pavement, the chemical properties of asphalt are considered. Asphalts produced from various refineries are anticipated to have different fraction components. Asphalt can be separated into five fraction components according to ASTM (D2006) [4].These fractions have functions [5] as shown below:

1. Asphaltenes (A): The portion that is insoluble in 50 volume of n-pentane. It acts as (bodying agent).
2. Polar compounds (PC): The nitrogen bases, the portion that is soluble in pentane and that reacts with cold 85% sulfuric acid. It serves as peptizer for asphaltenes (highly reactive resins).
3. First acidaffins (Al): The portion that does not react with cold 85% sulfuric acid, but does react with cold concentrated sulfuric acid. It functions as a solvent for peptized asphaltenes (more reactive-resinous hydrocarbons).
4. Second acidaffins (A2): The portion that does not react with cold concentrated sulfuric acid but does react with cold fuming (30% free SO_3) sulfuric acid. Silica gel is substituted for fuming acid precipitation. It acts as a solvent for peptized asphaltenes (less reactive-slightly unsaturated hydrocarbons).
5. Saturated hydrocarbons (S): The paraffin, the portion that does not react with cold fuming sulfuric acid or it is that one that is not adsorbed on silica gel, while all other components are adsorbed on silica gel. It serves as a gelling agent for the asphalt components.

Asphaltenes are soluble only in the polar compounds. First acidaffins and second acidaffins act as a medium to disperse the dissolved asphaltenes, and the saturated hydrocarbons (paraffin) develop the setting characteristics of the entire solution [6].

Asphalts can be also separated into four fractions according to ASTM (D4124) [7] defined as Saturates, Naphthene Aromatic, Polar Aromatics and nC_7 Asphaltenes, but the first procedure is considered as one of the uncomplicated methods for analyzing asphalts [8].

Apparatus and Materials

1. Adsorption Column, an 813mm (32 in.) Length of 20 mm o.d glass tubing with one end drawn to approximately 8 mm was constructed and prepared. A cotton absorbent plug was tamped in the bottom of the column followed by 43 g of silica gel; pore size 22°A, 28 to 200 mesh, 15g of silica gel; pore size 140°A, 60 to 200 mesh and finally 3-4 g of silica gel; pore size 140°A, 4 to 10 mesh. Each of them was tapped to settle respectively.
2. Distilling Apparatus (Rostler-Sternberg) was made of borosilicate glass.
3. Boiling water bath.
4. Water-cooled condenser.
5. Vacuum source, capable of reducing pressure in distilling apparatus to 15 mm Hg within 3 minutes.
6. Pentane, Sulfuric acid (98% reagent grade), Sodium hydroxide pellets.

All of these reagents and materials were provided from BDH Company.

Procedure

Five samples were taken from the refineries of Qayarah, Nassiriyah, Baiji, Samawah and Daurah for the work and analyzed according to ASTM (D2006) [4].

Determination of Asphaltenes.

1±0.1 g specimen was weighed into 100 ml weighing flask, warmed to distribute the specimen, cooled to room temperature, then 50 ml of n-pentane was added, swirled and allowed the mixture to stand for 15 hours. The mixture was filtered, rinsed with 10-20 ml pentane three times until the filter paper showed no oily ring. The filtrate was transferred into a previously weighed bulb and distilled.

When the distillation of solvent had ceased, the condenser was disconnected from the distilling apparatus while the bulb still immersed in the boiling bath, a vacuum suction was carefully applied to the apparatus till the foaming subsides. The bulb was separated, dried, cooled and weighed. The residue R_1 is the pentane-soluble portion of the specimen.

Determination of Polar Compounds

1±0.1 g of specimen was weighed, dissolved in 5 ml n-pentane and transferred quantitatively to 100 ml cylinder by rinsing with n-pentane until the volume of the solution was 20 ml then 2.5 ml of 85% H_2SO_4 was added. The cylinder was glass stoppered, covered with a cloth pad, grasped tightly and shaken hardly for 3 minutes.

The acid sludge was settled from the pentane solution by allowing the cylinder to stand for 2 hours. The n-pentane solution was then decanted into 250 ml flask, rinsing the cylinder twice with n-pentane and decanting into the 250 ml flask while the acid sludge was discarded. 20 g of sodium hydroxide pellets were added, swirled and allowed to stand a minimum of 20 minutes. The solution was filtered, rinsed with n-pentane until filter paper showed no oily ring. The solvent was distilled as mentioned previously (asphaltene determination).The residue R_2 is the fraction not reacting with 85% H_2SO_4 .

Determination of First Acidaffins

1±0.1 g of specimen was weighed, dissolved in 5 ml n-pentane then 2.5 ml of concentrated sulfuric acid was added, shaken, settled, decanted, neutralized with 20g of sodium hydroxide pellets and finally distilled and evaporated to dryness and weighed as above. The residue R_3 is the fraction not reacting with concentrated sulfuric acid.

Determination of Second Acidaffins and Saturated Hydrocarbons

1±0.1 g of specimen was weighed, dissolved in 20 ml n-pentane then passed into the silica gel at the top of the adsorption column and the effluent was received at the bottom of the column. The upper part of the column was rinsed with n-pentane till 100 ml of the effluent was collected. The collected n-pentane solution was distilled as above and the residue R_4 is the saturated portion of the specimen.

Calculations

$Q_1 = (R_1/S_1) \times 100$ ………………………………….(1)

Where

Q_1= percentage soluble in pentane

R_1= weight of pentane-soluble fraction,

g

S_1= weight of specimen used, g

$Q_2 = (R_2/S_2) \times 100$ …………………………………... (2)

Where

Q_2 = percentage not reacting with 85% H_2SO_4

R_2= weight of fraction not reacting with 85% H_2SO_4,

g S_2= weight of specimen used, g

$Q_3 = (R_3/S_3) \times 100$ ……………………………………. (3)

Where

Q_3= percentage not reacting with concentrated H_2SO_4

R_3= weight of fraction not reacting with concentrated H_2SO_4, g

S_3= weight of specimen used, g

$Q_4 = (R_4/S_4) \times 100$ ……………………………………. (4)

Where

Q_4= percentage not adsorbed on silica gel

R_4= weight of fraction not adsorbed on silica gel, g

S_4= weight of specimen used, g

Therefore the weight percentage of the components is as follows:

- Asphaltenes, % by weight= $100-Q_1$
- Polar Compounds, % by weight= Q_1-Q_2
- First Acidaffins, % by weight= Q_2-Q_3
- Second Acidaffins, % by weight= Q_3-Q_4
- Saturated Hydrocarbons, % by weight= Q_4

Results and Discussion

Table (2) demonstrates the results of chemical composition of the grades for both the original and aged asphalts. The precision and accuracy were calculated and expressed by the relative standard deviation (RSD %) and the relative error (RE %).

The results show that Qayarah asphalt with high asphaltenes content and relatively low-content of polar compounds exhibits a gel structure, while Nassiriyah asphalt with lower asphaltenes and higher content of polar compounds yields sol type asphalt. Syneresis, which is the incompatibility of asphaltenes with the acidaffins and saturated hydrocarbons, is governed by the ratio PC/S (polar compounds/ saturated hydrocarbons). Therefore, asphaltenes content and the ratio of PC/S are considered responsible for the rheological properties of asphalt sol-gel characteristics [9, 10].

It was reported that during aging process an increase in the asphaltene fraction of asphalt is occurred except Baiji asphalt (almost constant), and as a result, the ratio of maltenes to asphaltenes is reduced causing dry and brittle asphalt and this may be clue to the conversion of maltene components to asphaltene components [5].

The PC/S ratio of original and aged asphalt produced from the various refineries is shown in table (3); it varies between (0.76-2.58) for original asphalt. Baiji asphalt shows the lowest ratio while Nassiriyah and Daurah asphalts show the highest. After aging the (PC/S) ratio is altered to range between (1.08-2.60).The ratio PC/S must be 0.5 or greater to assure these components will not separate [6, 11].

The Durability Rating (Rostler and White parameter), (PC+A1/S+A2), defined as the ratio of the more reactive to the less reactive fractional components in asphalt is shown also in table (3). The Durability Rating values vary between (0.83-1.92) for original asphalt, but altered to (1.02-1.78) after aging. The asphalt durability increases with the decrease in Durability Rating .The Qayarah asphalt is considered as the least durability grade.

Rostler and White, mentioned that asphalt with Durability Rating not exceeding (1.5) is considered to be satisfactory [12]; while the issue of TRICOR Refining, LCC and the specification of the City of Lafayette (USA) considered the limitation between (0.2-1.2) to assure good aging properties [5,11].

Conclusion

The analysis covers determination of the composition of asphalt in terms of components that are characterized by specific chemical reactivity. The determination of second acidaffins and saturated hydrocarbons by the adsorption method has been found to be suitable for asphalt. The five groups of components (asphaltenes, polar compounds, first acidaffins, second acidaffins and saturated hydrocarbons) give better understanding of (PC/S) ratio, asphalt durability and rheological properties of asphalt. The durability of asphalt depends upon the ratio (PC+A1/S+A2) as determined by ASTM method D2006.

During the process of aging, the ratio of maltenes (the remainder of the asphalt material left after precipitation of the asphaltenes) to asphaltenes is reduced, resulting in being dry and brittle asphalt pavement.

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Table (1): Some physical properties of original grades of asphalt and asphalt after aging

Physical properties of asphalt	Qayarah asphalt	Nassiriyah asphalt	Baiji asphalt	Samawah asphalt	Daurah asphalt
Original asphalt					
Penetration; 1/10mm 25°C, 100g, 5 sec	43	41	43	46	45
Absolute Viscosity at 60°C, poises	5265	4420	4112	3150	2065
Specific Gravity	1.053	1.028	1.028	1.022	1.051
Aging asphalt					
Penetration; 1/10mm	24	28	22	28	31
Absolute Viscosity at 60°c, poises	10550	9785	9064	5022	2637
Mass Loss, %	0.56	0.02	-------	0.10	0.58

Table (2): Chemical fraction of the asphalt grades for both the original and after aging

Chemical Fraction	Qayarah asphalt	Nassiriyah asphalt	Baiji asphalt	Samawah asphalt	Daurah asphalt
Original asphalt					
Asphaltene	39.95	24.91	30.41	27.43	22.3
RE%±	0.15	0.12	0.21	0.20	0.31
RSD%	0.19	0.15	0.25	0.24	0.36
Polar compounds	16.51	33.34	15.07	26.96	25.31
RE%±	0.57	0.66	0.29	0.18	0.39
RSD%	0.81	0.87	0.42	0.22	0.53
First acidaffins	23.03	13.77	16.62	16.37	20.22
RE%±	0.15	0.49	0.30	0.21	0.56
RSD%	0.20	0.65	0.36	0.29	0.76
Second acidaffins	7.52	15.09	18.22	14.75	21.80
RE%±	1.06	0.38	0.31	0.13	0.33
RSD%	1.35	0.46	0.38	0.19	0.40
Saturates	12.99	12.89	19.68	14.49	10.37
RE%±	0.34	0.33	0.31	0.17	0.21
RSD%	0.45	0.40	0.47	0.21	0.26
Aging asphalt					
Asphaltene	40.5	30.13	29.87	31.00	24.82
RE% ±	0.15	0.16	0.23	0.17	0.19
RSD%	0.19	0.22	0.32	0.20	0.26
Polar compounds	29.79	23.89	21.10	32.47	27.39
RE%±	0.16	0.11	0.32	0.18	0.17
RSD%	0.23	0.13	0.40	0.23	0.27
First acidaffins	8.35	14.87	14.37	9.44	17.21
RE%±	0.39	0.25	0.20	0.18	0.13
RSD%	0.44	0.33	0.25	0.21	0.16
Second acidaffins	6.41	15.37	15.28	10.41	20.05
RE%±	0.35	0.21	0.19	0.43	0.35
RSD%	0.43	0.26	0.26	0.50	0.40
Saturates	14.95	15.74	19.38	16.68	10.53
RE%±	0.25	0.19	0.11	0.16	0.28
RSD%	0.29	0.25	0.14	0.22	0.42

Table (3): Parameters of original and oven-aged asphalt produced from various refineries

Parameters	Qayarah asphalt	Nassiriyah asphalt	Baiji asphalt	Samawah asphalt	Daurah asphalt
Original asphalt					
PC/S	1.27	2.58	0.76	1.86	2.44
Durability Rating PC+A1/S+A2	1.92	1.68	0.83	1.48	1.41
Aging asphalt					
PC/S	1.99	1.51	1.08	1.94	2.60
Durability Rating PC+A1/S+A2	1.78	1.24	1.02	1.54	1.45

التحليل الكيميائي التجزيئي للاسفلت دالة لقوة تحمله

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الخلاصة

لغرض الحصول على مفهوم أفضل لاداء الاسفلت المستعمل في أعمال التبليط فقد أجري التحليل الكيميائي التجزيئي لخمسة نماذج مأخوذة من مصافي العراق الخمسة (القيارة، الناصرية، بيجي، السماوة والدورة) التي تضمنت مكونات:
(asphaltenes, polar compounds, first acidaffins, second acidaffins and saturated hydrocarbons)
وتدعى المقاطع الاربعة الاخيرة maltenes

تم استخراج كل من polar compounds/saturated hydrocarbons (PC/S) ونسبة التحمل التي تمثل نسبة المقاطع التجزيئية الفعالة الى المقاطع التجزيئية غير الفعالة للـ maltenes لكل أنموذج أسفلت.لقد بينت الدراسة أن الاسفلت المنتج في مصفى بيجي كان أفضل أنواع الاسفلت تحملا من غيره من أنواع الاسفلت الاخرى المنتج في باقي المصافي العراقية فيما عد أسفلت القيارة أقلهم درجة تحمل.

ان النتائج المستحصلة أكدت أن العلاقة بين المكونات الكيميائية للاسفلت تعد دالة لقوة تحمل الاسفلت ومن ثم تعطينا مفهوما أفضل لاداء الاسفلت.