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The Effect of Saturates on Rheological and Aging Characteristics of Bitumen

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***Abstract*—**According to Rostler method (ASTM D 2006), saturates content of bitumen is determined based on its reactivity to sulphuric acid. While Corbett method (ASTM D 4124) based on its polarity level. This paper presents results from the study on the effect of saturates content determined by two different fractionation methods on the rheological and aging characteristics of bitumen. The result indicated that the increment of saturates content tended to reduce all the rheological characteristics concerned. Bitumen became less elastic, less viscous, and less resistant to plastic deformation, but became more resistant to fatigue cracking. After short and long term aging process, the treatment effect coefficients of saturates decreased, saturates became thicker due to aging process. This study concludes that saturates is not really stable or reactive in aging process. Therefore, the reactivity of saturates should be considered in bitumen aging index.

***Keywords*—**Aging index, bitumen, saturates, rheolgy.

I. Introduction

THEORETICALLY, bitumen characteristics are formed by the characteristics of each chemical component hence the chemical composition of bitumen is useful in evaluating and modifying bitumen composition to produce better physical and rheological characteristics bitumen. Bitumen consists of thousand types of hydrocarbon molecules. It is impossible to analyse them individually therefore, chemical composition of bitumen usually analysed through fractionation. Bitumen is divided into a number of fractions. Each fraction consists of molecules with similar characteristics. For examples, Rostler divided bitumen into five fractions which are asphaltenes, nitrogen bases, first acidaffins, second acidaffins, and saturates. While Corbett divided bitumen into four fractions *i.e.* asphaltenes, polar aromatics, naphthene aromatics, and saturates. The fractionation procedure introduced by Rostler and Corbett were standardized as ASTM D 2006 and D 4124 respectively.

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This paper presents the result from the study on the effect of saturates content determined by the two different fractionation methods on the rheological and aging characteristics of bitumen. Saturates is as a jelling agent for the bitumen components [1]. The saturates fraction also known as paraffins fraction, is a mixture of pure aliphatics, aliphatics with side chines, cycloaliphatics, and cycloaliphatics with side chines [2].

Increasing saturates content is expected to decrease the complex shear modulus and increase the phase angle of bitumen, because saturates fraction is a lightest part of malthen, hereas malthnes is a liquid part of bitumen which complements with solid asphaltenes.

On the other hand, because paraffins content in bitumen is relatively constant during aging process, many researchers concluded that the paraffins is a stable component, so that its contribution to rheological bitumen is also constant during aging process [3] [4]. However, most studies in the past considered the stability of the chemical component in term of content instead of rheological characteristics. Although the content of paraffins is constant during aging process, its rheological characteristic might change. This paper aims to address this issue by quantifying the effect of saturates on rheology of bitumen at various stages of aging process.

II. Materials and Method

The materials used in this study are Buton rock asphalt (BRA) from Lawele Region, Indonesia and petroleum bitumen penetration grade 80/100 form Kemaman refinery, Malaysia. Bitumen of Buton rock asphalt was extracted and recovered in accordance of ASTM D 2172 and ASTM D 5404 respectively. Characteristics of each material are shown in Tables I to III.

TABLE I
CHARACTERISTICS OF RAW MATERIAL OF BUTON ROCK ASPHALT

Lawele-BRA Characteristics	Test method	Test results
Bitumen content; %	ASTM D 2172	35.3
Water content; %	ASTM D 1461	11.8
Penetration of extracted bitumen at 25°C, 100g, 5 sec; dmm	ASTM D 5	183
Loss on heating of dry B.R.A. (TFOT); %	ASTM D 1754	6.1

Saturates from the bitumen of the Buton rock asphalt and the petroleum bitumen were extracted based on ASTM D 2006 and ASTM D 4124 testing procedures. Extraction process of each method is illustrated in Figs. 1 and 2.

TABLE II
CHARACTERISTICS OF BITUMEN OF BUTON ROCK ASPHALT

Characteristics	Test method	Test results	Specification *)
Penetration at 25 °C, 100 g, 5 sec; 0,1; mm	ASTM D 5	85	80 – 100
Ductility at 25 °C, 5 cm/minute; Cm	ASTM D 113	>140	Min. 100
Loss on heating (RTFOT); %	ASTM D 2872	1.53	0.8
Penetration at 25 °C, 100 g, 5 sec after RTFOT; % Original	ASTM D 5	65.2	Min. 47
Ductility at 25 °C, 5 cm/minute after RTFOT, cm	ASTM D 113	>140	Min. 75
Solubility in C_2HCl_3; %	ASTM D 2042	99.2	Min. 99
Water content; %	ASTM D 1461	0.00	-

*) The specification refers to ASTM D 946

TABLE III
PETROLEUM BITUMEN PEN 80/100 CHARACTERISTICS

Petroleum Bitumen Characteristics	Test method	Test results	Specification*)
Penetration at 25 C, 100 g, 5 sec; dmm	ASTM D5	95	80 – 100
Ductility at 25 °C, 5 cm/minute; cm	ASTM D113	>140	Min. 100
Loss on heating (RTFOT); %	ASTM D2872	0.035	0.8
Penetration at 25 C, 100 g, 5 sec after RTFOT, % Original	ASTM D5	76.9	Min. 47
Ductility at 25 °C, 5 cm/minute, after RTFOT; cm	ASTM D113	>140	Min. 75
Solubility in C_2HCl_3; %	ASTM D1461	99.5	Min. 99
Water content; %	ASTM D2042	0.0	-

*) The specification refers to ASTM D 946

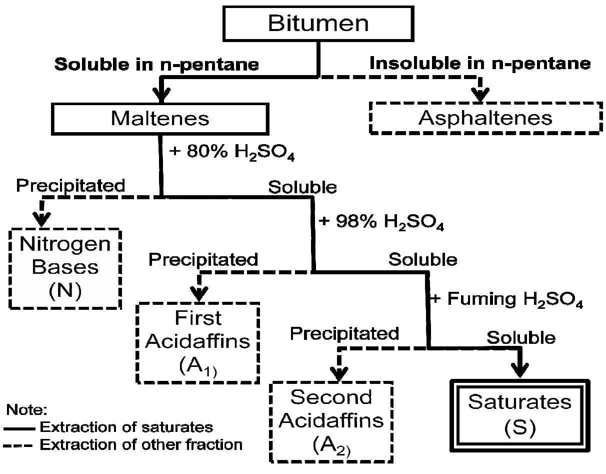

Fig. 1 Separating bitumen component based on ASTM D 2006 (Rostler method)

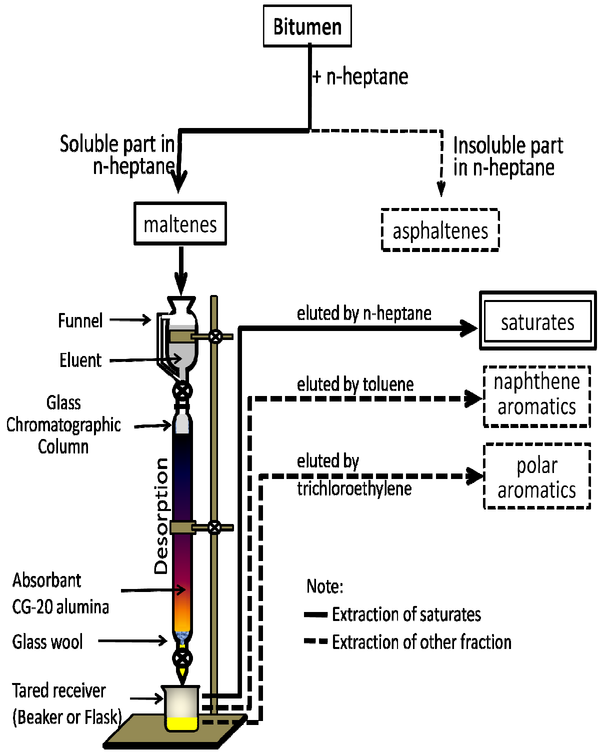

Fig. 2 Separating bitumen component based on ASTM D 4124 (Corbett method)

Based on ASTM D 2006, the bitumen sample was dissolved in n-pentane. The solution was then filtered to remove the insoluble part (asphaltenes). The maltenes solution reacted with H_2SO_4 of different concentration to precipitate the other fractions as follow: Nitrogen bases were precipitated by using H_2SO_4 solution at 85% concentration. First acidaffins was precipitated using H_2SO_4 solution at 98% concentration, and second accidaffins was precipitated using fuming H_2SO_4. After filtering, the soluble saturates was recovered by evaporating the solvent through heating process at 105°C.

Based on ASTM D 4124, the bitumen sample was dissolved in n-heptane. Then, the solution was filtered to remove the asphaltenes. The maltenes solution which consisted of saturates, naphthene aromatics and polar aromatics, was poured into the column chromatography to be absorbed by CG-20 Alumina. The saturates fraction was eluted by n-heptane and recovered by evaporating the solvent through heating at 105°C.

Each extracted saturates was blended in proportions of 0%, 5%, and 10% with the Kemaman petroleum bitumen as a bitumen medium. The blended bitumens were tested for rheological characteristics using Dynamic Shear Rheometer or DSR (ASTM D 7175). DSR test measured the complex shear modulus G*, and the phase angel δ of bitumen. These two parameters are used in Superpave Performance Grade Specification to determine rutting and fatigue resistance of bitumen binder. The specification has been standardized as standard specification for performance grade asphalt binder

ASTM D 6373-07e-1.

Samples were tested at five different temperature (46°C, 52°C, 58°C, 64°C and 70°C) and at un-aged, RTFOT-aged (artificial short-term aged) and PAV-aged (artificial long-term aged) conditions. This range of temperature is equal to the range of maximum bitumen performance grade temperature (ASTM D 6373).

Superpave chooses G*/sin[δ] parameter as rutting factor to indicate rutting resistance of bitumen because this parameter determined the work dissipated per load cycle at a constant stress related to thge behaviour of asphalt [5]. Parameter G*sin[δ] is selected as fatigue factor since this parameter determined the work dissipated per load cycle at a constant strain which considered as relevance to fatigue behaviour of the asphalt under a constant strain condition [5]. It is worth to notice that G*sin[δ] is actually equal to the viscous modulus G".

The test results were assumed as normal and homogenous because the experiment was conducted in homogenous environment where the level factors interaction was controlled.

The relationship of the saturates content with the rheological characteristics of blend bitumen was evaluated statistically using analysis of variants (ANOVA), and analysis of regression. ANOVA was used to evaluate the significant effect of factors on variants, and analysis of regression was used to determine the coefficient regression. Five factors (independent variables) are exhibited in the following table.

TABLE IV
FACTORS AND THE LEVEL FACTORS

Factor	Level factor
Source of saturates	BRA-bitumen, and petroleum bitumen
Method of extracting saturates	Rostler method, and Corbett method
Percentage of saturates	0%, 5%, and 10%
Test temperature	46°C, 52°C, 58°C, 64°C, and 70°C
Aging condition	Un-aged, RTFOT-aged, and PAV-aged

The variants (dependent variables) were rheological characteristics of bitumen which consist of G*, δ, G', G", and G*/sin[δ]. However, only G* and δ were used in ANOVA because the remaining variants were merely a derivative of G* and δ. Variants in regression analysis where G', G", and G*/sin[δ]. These three variants were directlt related to the bituminous mixture performance.

III. RESULT AND DISCUSSION

The data analysis results by factorial strip plot design are shown in Tables V and VI. In ANOVA, the H_0 hypothesis was the source of variant which does not yield any significant effect, and H_1 hypothesis was the source of variant with significant effect. For 95% confidence level, the critical point of significant value (α) is 0.05. H_0 was rejected if the significant value was less than 0.05, and H_0 was accepted if the significant value was more than 0.05.

TABLE V
THE ANALYSIS OF VARIANTS OF THE EFFECT OF THE SATURATES FRACTION ON COMPLEX SHEAR MODULUS (G*)

Source of variant	df	Type III Sum of Squares	Mean Square	F	Significant
Sources of saturates	1	760551	760551	0.06	0.805 *)
Method of extraction	1	1.927E8	1.927E8	15.49	0.000
Percentage of saturates	2	2.505E9	1.253E9	100.70	0.000
Test temperature	4	1.083E10	2.709E9	217.73	0.000
Aging condition	2	8.022E9	4.011E9	322.42	0.000
Error	379	4.715E9	1.244E7		
Total	390	3.758E10			

Note: *) Not significant

TABLE VI
THE ANALYSIS OF VARIANTS RESULTS OF THE EFFECT OF THE SATURATES FRACTION ON PHASE ANGLE (Δ)

Source of variant	df	Type III Sum of Squares	Mean Square	F	Significant
Sources of saturates	1	0.015	0.015	0.004	0.947 *)
Method of extraction	1	121	121	35.92	0.000
Percentage of saturates	2	118	59	17.40	0.000
Test temperature	4	2479	620	183.36	0.000
Aging condition	2	7965	3982	1178.17	0.000
Error	379	1281	3.380		
Total	390	2669570			

Note: *) Not significant

The results indicate that the source of saturates has significant value of 0.805 or larger than the critical point value 0.05. There was no difference in effect of saturates from either Buton rock asphalt or petroleum bitumen on the complex shear modulus G*. The other factors have significant value less than 0.05, which means that different factor caused different value of G*.

Table VI exhibits that all source of variant, except for the source of saturates, significantly influenced the phase angel.

Because there was no effect fram source of saturates, this factor was excluded in the regression analysis. Therefore the selected independent variables were the percentage of saturates, test temperature, and aging conditions. These variables were regressed to dependent variables which consisted of G', G", and G*/sin[δ].

The result yielded the exponential regression model of saturates content with bitumen rheological characteristic. The model was transformed into a linear model by expressing the bitumen rheological characteristics in the natural logarithmic values. The regression model is shown in Equation 1.

$$\text{Ln } Y = a X_1 + bX_2 + c \quad (1)$$

where: Y = rheological characteristics; X_1 = percentage of saturates; X_2 = temperature; a, b, and c = coefficient of X_1, X_2, and Constant.

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The model was analysed statistically using two indicators. They were:

(i) Significant level of regression, and
(ii) Coefficient determination of regression (R).

The significant level of regression indicated the probability that the functional relationships real. The significant value of regression less than 0.05 indicates 95% chance that the relationship exists. The coefficient of determination (R^2) shows how well a regression model fits the data. It represents the percentage of variation that could be explained by the regression equation. The analysis results of the regression models of the bitumen rheological at fresh, different levels of aging, and different methods of extraction, are shown in Tables VII and VIII.

TABLE VII
ANALYSIS OF THE REGRESSION MODEL OF THE SATURATES CONTENT (EXTRACTED BASED ON ROSTLER METHOD) ON BITUMEN RHEOLOGY

Rheological Characteristics (Y)	R	a	b	c	Significant of Regression
Un-aged Condition :					
Ln G'	0.993	-0.114	-0.208	17.240	0.000
Ln G"	0.994	-0.095	-0.141	16.127	0.000
Ln (G*/sin[δ])	0.994	-0.095	-0.141	16.175	0.000
Short Term Aging (after TFOT) Condition :					
Ln G'	0.996	-0.038	-.0.195	17.950	0.000
Ln G"	0.998	-0.045	-0.133	16.417	0.000
Ln (G*/sin[δ])	0.998	-0.045	-0.135	16.563	0.000
Long Term Aging (after PAV) Condition :					
Ln G'	0.938	-0.004	-0.185	19.557	0.000
Ln G"	0.972	-0.031	-0.128	17.432	0.000
Ln (G*/sin[δ])	0.974	-0.026	-0.136	17.946	0.000

Note: Y = rheological characteristics, X_1 = percentage of saturates, X_2 = test temperature, a = coefficient of X_1, b = coefficient of X_2, c = Constant,

TABLE VIII
ANALYSISOF THE REGRESSION MODEL OF THE SATURATES CONTENT (EXTRACTED BASED ON CORBETT METHOD) ON BITUMEN RHEOLOGY

Rheological Characteristics (Y)	R	a	b	c	Significant of Regression
Un-aged Condition					
Ln G'	0.998	-0.218	-0.203	16.936	0.000
Ln G"	0.998	-0.159	-0.138	15.948	0.000
Ln (G*/sin[δ])	0.998	-0.160	-0.139	15.988	0.000
Short Term Aging (after TFOT) Condition					
Ln G'	0.999	-0.150	-0.197	18.017	0.000
Ln G"	0.999	-0.114	-0.136	16.515	0.000
Ln (G*/sin[δ])	0.999	-0.115	-0.138	16.649	0.000
Long Term Aging (after PAV) Condition					
Ln G'	0.998	-0.127	-0.180	19.442	0.000
Ln G"	0.998	-0.096	-0.131	17.721	0.000
Ln (G*/sin[δ])	0.998	-0.099	-0.136	18.081	0.000

Note: Y = rheological characteristics, X_1 = percentage of saturates, X_2 = test temperature, a = coefficient of X_1, b = coefficient of X_2, c = Constant.

Tables VII and VIII showed that all of the coefficients determination at un-aged, RTFOT aged, and PAV aged; were in the range of 0.938 to 0.999. Regression models can explain the relationship between the rheology of bitumen and its saturates content very well. Furthermore, all of the significant regression values indicate the functional relationships of the regression models are real.

The effect of different method of saturates extraction on the bitumen rheology is shown in Fig. 3.

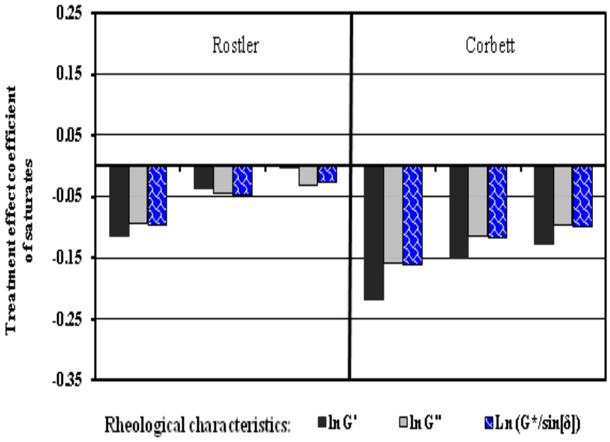

Fig. 3 The treatment-effect-coefficient of saturates in the regression equations

The results showed that under the same aged condition, the two different methods yielded treatment effect coefficient of different magnitude. This indicated that both methods produced saturates with different characteristics. However, the rate of change of the coefficient of both samples followed the same decrease trend with aging due to saturates hardening. Theoretically, since the saturates consisted of pure aliphatic or saturated molecules, it would never be aged except in the presence of ozone, halogen at high temperature or ultraviolet. In contrast, Fig. 3 indicates that during RTFOT-aging and PAV-aging process, the treatment effect coefficient of saturates on the bitumen rheological characteristics increased gradually. The most probable explanation for this phenomenon was that saturates do not consist of pure aliphatic hydrocarbon alone. Instead, there were molecules connected with the other reactive molecules such as carbonyl, sulfoxide, and un-saturated hydrocarbon molecules in a small proportion. It is in line with Michalica *et al* data which found that nitrogen, sulphur, and oxygen also existed in the saturates [5]. It was also reported that hydrogen to carbon ratio (H/C) was less than two, which indicated the existence of un-saturated hydrocarbon molecules.

The saturates fraction produced by Rostler method indicated that saturates has aged even just after the initial extraction process which might resulted from the use of sulphuric acid of various concentration levels in the extraction process. It is well known that sulphuric acid may act as an acid, as an oxidizing agent, and as a hydrating agent. The extracted saturates was thicker due to the oxidization and dehydration process from the use of sulphuric acid.

In contrast, the saturates fraction extracted based on Corbett method was in fresher condition because the extraction was based on solubility in various solvent at different polarity levels hence no chemical reaction was involved.

The effect of test temperature on the rheological characteristics at various level of aging was compared and presented in Fig. 4.

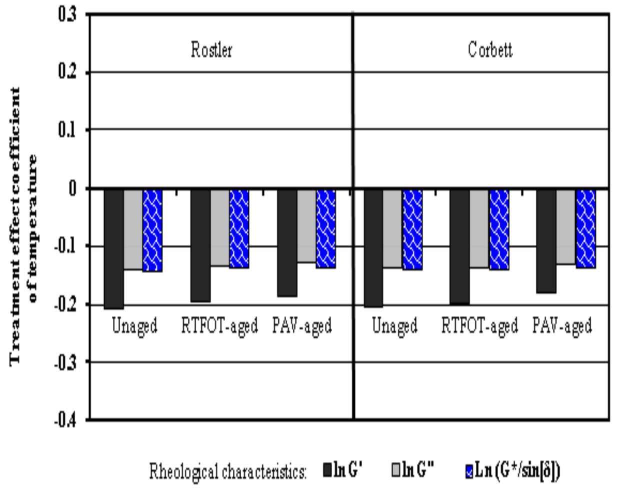

Fig. 4 Comparison of The treatment-effect-coefficient of temperature on the bitumen rheological characteristics in the regression equations

The result indicated that the effect of test temperature on the bitumen rheological characteristic of samples containing the saturates produced by two different methods of extraction was similar since both samples were prepared with the same bitumen medium. All treatment-effect-coefficient of test temperature on bitumen rheological characteristics at all aging conditions were negative. As temperature increased, the bitumen rheological characteristics decreased. Furthermore, the absolute value of the treatment-effect-coefficient of test temperature on the elastic modulus was higher than the viscous modulus deducing the conclusion that temperature increment affected elastic modulus more than viscous modulus. Fig. 4 also demonstrated that at long-term aging condition bitumen became less susceptible to temperature.

The constant of the regression equations based on both Rostler and Corbett fractionation methods presented and compared as exhibited in Fig. 5.

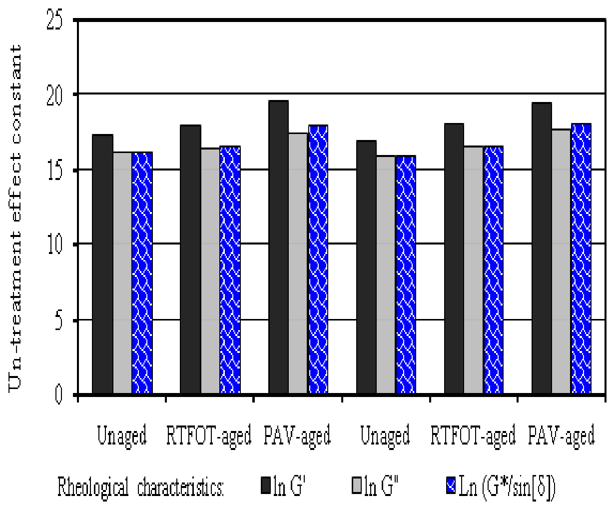

Fig. 5 Comparison of the un-treatment effect coefficient in the regression equations

The un-treatment effect coefficient constant indicated the rheological characteristics of the bitumen medium used in the experiment. As mentioned earlier, the experiment used same petroleum bitumen; therefore, it is imperative that the un-treatment-effect-coefficient constant between two regression equation models were relatively same as shown in Fig. 5.

Aging characteristics of bitumen can be identified by aging index (AI) which is defined as the ratio of a bitumen chemical or rheological parameter after and before aging [6] [7]. The aging index based on rheological characteristics was calculated by the following equations.

$$\mathrm{AI} = \frac{(\text{Aged bitumen rheology})}{(\text{Unaged bitumen rheology})} \quad (2)$$

$$\ln \mathrm{AI} = \ln(\text{Aged bitumen rheology}) - \ln(\text{Unaged bitumen rheology}) \quad (3)$$

Contribution of saturates fraction on bitumen aging index was calculated by substituting Equation 1 into Equation 3 as follow.

$$\ln \mathrm{AI} = (aX_1 + bX_2 + C)_{aged} - (aX_1 + bX_2 + C)_{unaged} \quad (4)$$

or,

$$\ln \mathrm{AI} = (a_{aged}-a_{unaged})X_1 + (b_{aged}-b_{unaged})X_2 + (c_{aged}-c_{unaged}) \quad (5)$$

The aging index are differentiated based on its level of aging as short and long term aging indices. The aging index for G', G", and G*/sin[δ] are shown in Figs. 6 to 8. The results indicated that, the increment of saturates increased ln AI. As expected, PAV aged bitumen yield a higher Aging Index than RTFOT aged bitumen.

With refference to Equations 5, contribution of saturates on ln AI is defined as (a_{aged} - a_{unged}) and the results are shown in Table IX. Only extracted saturates based on Corbett method are considered and presented. The saturates fraction based on Rostler method were not counted because it was considered as oxidized and dehydrated.

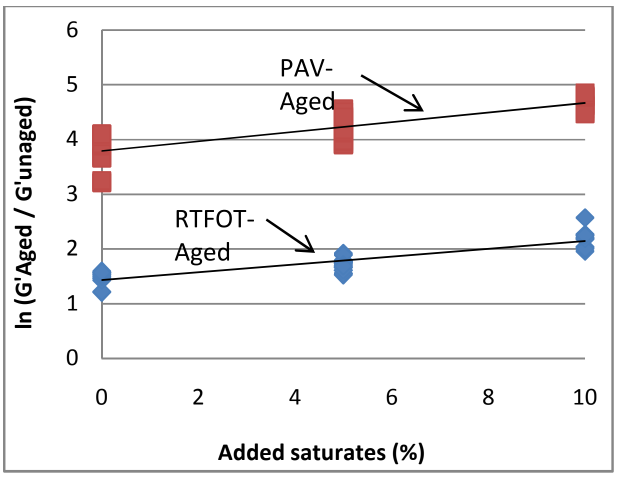

Fig. 6 Logarithmic Aging Index for G' of the blended bitumen

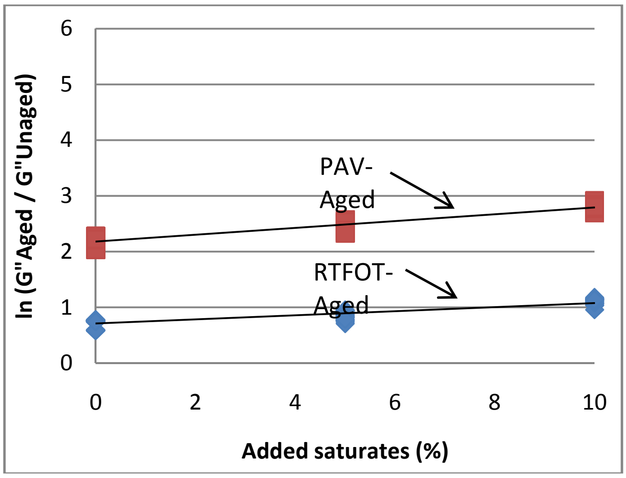

Fig. 7 Logarithmic Aging Index for G” of the blended bitumen

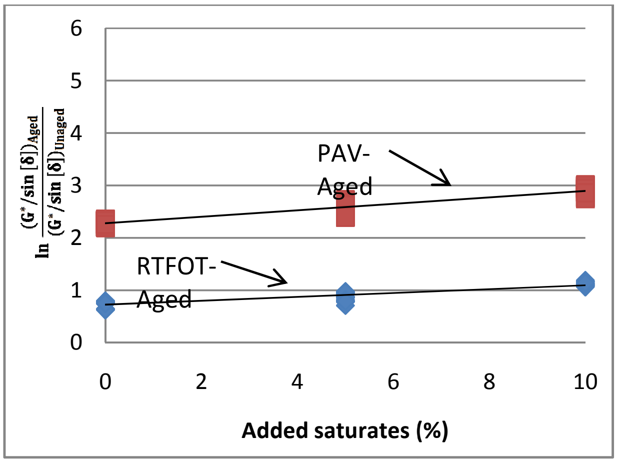

Fig. 8 Logarithmic Aging Index for G*/sin[δ] of the blended bitumen

TABLE IX
CONTRIBUTION OF SATURATES FRACTION (CORBETT) ON BITUMEN AGING INDEX

Aging Type	Contribution of each additional percentage of saturates fraction into bitumen medium on logarithmic of Bitumen Aging Index		
	ln G’	ln G”	ln (G*/sin[δ])
	(a_{aged} - a_{unaged})	(a_{aged} - a_{unaged})	(a_{aged} - a_{unaged})
Short-Term Aging (RTFOT)	0.068	0.045	0.045
Long-Term Aging (PAV)	0.091	0.054	0.061

IV. CONCLUSION

Rostler and Corbett methods of bitumen fractionation were employed in the study. The result indicates that two different methods yield saturates with different characteristics. The Corbett method was preferred since it yielded fresher saturates with no oxidization and dehydration involved during the fractionation process. A number of regression models were developed to analyse the effect of saturates content on the rheological characteristics of bitumen. The result indicated that the increment of saturates content tend to reduce all the rheological characteristics concerned. Bitumen becomes less elastic, less viscous, and less resistant to plastic deformation, but becomes more resistant to fatigue cracking. After short and long term aging process, the treatment effect coefficients of saturates decreased and became thicker due to aging process. It concludes that saturates is not really stable or reactive in aging process as previously assumed. Therefore, the saturates should be considered and included in bitumen aging index.

ACKNOWLEDGMENT

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