Zero shear viscosity from oscillation tests on aged and non-aged bitumens

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ABSTRACT

Bitumens are complex mixtures of hydrocarbons that show a wide range of molecular weights. This makes bitumens to behave as viscoelastic materials, whose mechanical response depends on the magnitude of the loads that are applied on them, as well as on the time and temperature the loads are applied. Quality specifications for bitumens have been developed in order to provide rational parameters for the bitumen resistance to rutting, cracking and ageing under service conditions. Some parameters based on the complex shear modulus that are already in use, have shown limitations when evaluating and comparing the bitumens resistance to rutting. On the other side, the zero shear viscosity has shown satisfactory correlation for the rutting resistance of bitumens in pavements. This work presents the determination of zero shear viscosity for two Colombian bitumens, compared to Boscan bitumen. Each bitumen was tested in three different ageing level (initial, rolling thin film ageing and pressure vessel ageing). Master curves for complex viscosity versus frequency were obtained by oscillation tests, and master curves data were fitted to three rheological models (Carreau, Cross-Sibilsky and Cross-Williamson), by using the least squares error method. Other parameters from the models were also estimated. It was found that zero shear viscosity depends on the ageing level of the bitumen, while the dependence on the type of bitumen is not significant. Besides, the three models can describe properly the relationship between complex viscosity and frequency. The results show that zero shear viscosity can be used as a parameter in quality specification for the three bitumens studied.

Keywords: Ageing, Rheology, Testing, Zero Shear Viscosity

1. INTRODUCTION

Bituminous binders constitute a heavy oil fraction, whose properties depend on their chemical composition and their structural features on the molecular level. In turn, these properties depend on the crude source and the process for producing the bitumen. In order to understand the behaviour of these materials, a number of studies have been done to stablish the relationships between the structural and functional features, with the physical properties of bitumen.

The importance of the heavy fractions of oil has been increasing due to the growing economy of heavy crudes and residues, as well as the progress that has been achieved for their analysis. The impact of these studies resides on that most of the oils that are being processed are heavy. Then, there are research trends that focus on heavy oil derivatives and optimization applications.

Most of bitumen applications include roads, waterproofing and coatings. Proper use of bitumen depends on the knowledge about their properties. In the early XX century, simple tests such as penetration, ductility and softening point were considered to classify bitumen. Later, viscosity was included as a fundamental property. However, research proved that discrete measurements of viscosity were not enough for describing the behavior of bitumen, which show viscoelastic properties that are strongly dependent on the time for external loads. As a result, dynamic rheological measurements are included in bitumen specification.

This document presents the Zero Shear Viscosity (ZSV) evaluation for three straight run bitumen (two of them produced in Colombia, and the third one produced in Venezuela). ZSV was also calculated for acceleratedly aged samples of each bitumen. The accelerated aging was carried out according to the standard procedures for Rolling Thin Film Oven Test (RTFOT) and Pressure Aging Vessel (PAV), from the Superpave specification for Bitumen. The ZSV was obtained by a Least Square Fitting from the Complex Shear Viscosity master curves for each sample. These Shear Complex Viscosity master curves were obtained by oscillatory tests. The models considered for the Least Square Fitting were the Cross-Williamson, Cross-Sybilski and Carreau models.

The ZSV is the viscosity measured at a near-to-zero shear. This concept is related to substances which viscosity depends on the shear velocity, the time that the shear stress is applied, and the temperature. In these cases, a discrete measurement of viscosity (obtained by using a viscometer, for example) is not enough to describe the rheological behaviour of those substances, which are known as complex rheological behaviour substances. This complex behaviour is not only present in bitumen, but also in paints, polymers, pastes and others. The ZSV has been included in the bitumen specification, since it is an indicator for their stiffness and resistance to permanent deformation.

ZSV can be estimated by performing two types of tests: oscillatory tests and creep compliance tests. In the oscillatory test, the ZSV is obtained by extrapolating the complex viscosity to a low frequency, while in the creep compliance test, it can be obtained as the steady state viscosity for a low shear stress. Depending on the type of the binder, the steady state is reached after a short or after a long time.

The models used in this work for estimating the ZSV value are the ones proposed by Carreau, Cross-Williamson and Cross-Sybilski, wich are described next:

Carreau Model

$$\eta^* = \frac{\eta_0 - \eta_\infty}{[1+(K\omega)^2]^{m/2}} + \eta_\infty \qquad (1)$$

Where η^* is the complex viscosity, η_0 is the viscosity at the first Newtonian region (which corresponds to the ZSV), η_∞ is the viscosity at an infinitum shear, ω is the reduced frequency (rad/s), K and m are parameters of the specific material.

Cross-Williamson Model

$$\eta^* = \frac{\eta_0 - \eta_\infty}{1+(K\omega)^m} + \eta_\infty \qquad (2)$$

The parameters have the same meaning as in the model proposed by Carreau.

Cross-Sybilski Model

$$\eta^* = \frac{\eta_0}{1+(K\omega)^m} \qquad (3)$$

The parameters have the same meaning as in the model proposed by Carreau.

2. EXPERIMENTAL

The samples were the bitumen produced in Apiay Refinery (Colombia), Barrancabermeja Refinery (Colombia) and Boscan (Venezuela). A strain controlled dynamic shear rheometer was used to do the measurements. Rheological measurements were conducted on the samples in their initial state, RTFOT aged samples, and RTFOT+PAV aged samples, for a total of nine samples. Strain sweeps were done to determine the limit strain for the linear viscoelastic region, at each temperature (-5, 5, 15, 25, 35, 45, 55, 65 and 75°C, representing the temperature span in Colombia). Frequency sweeps were done at each temperature by fixing the strain for viscoelastic region. Master curves were obtained by the time-temperature superposition principle, by fixing the 25°C curve as the reference temperature, and then the parameters of each model were estimated by least square fitting. This way, ZSV values were obtained for each model, and for each aged and unaged sample.

3. RESULTS AND DISCUSSION

Figure 1 shows the master curves for complex viscosity vs reduced frequency, for Apiay (figure 1.a), Barrancabermeja (figure 1.b) and Boscan (figure 1.c) bitumen, each one in their initial, RTFOT and RTFOT+PAV aged condition.

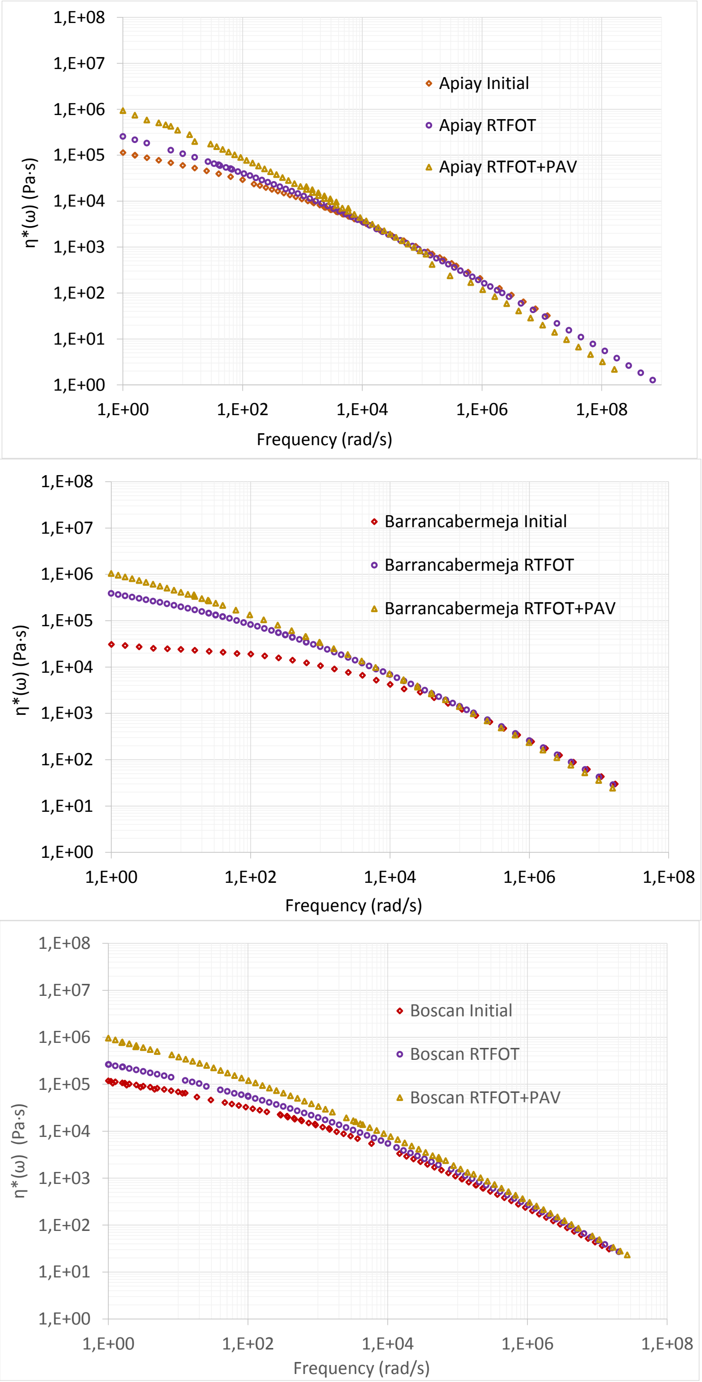

Figure 1: Master curves for complex viscosity at 25°C, in Apiay, Barrancabermeja and Boscan bitumen, each one in their initial, RTFOT aged and RTFOT+PAV aged condition.

It is observed that, for each bitumen, viscosity at low frequencies (~1 rad/s) depends on the aging level of the bitumen. It is also observed that the values of the complex viscosity vary from 10^5 to 10^6 Pa.s, for a 1 rad/s reduced frequency, excepting Barrancabermeja bitumen which, in its unaged condition, has a complex viscosity lower than 10^5 Pa.s. Another characteristic behaviour in the master curves for complex viscosity is the asymptote at the highest frequencies of the master curves. The master curves showed in the figure 1 correspond to the central part of a sigmoidal function that has a characteristic constant value at low frequencies that can be extrapolated from the data measured in the experiments. Figure 2 shows the fitting for each model and for the three ageing levels for Apiay bitumen. Crosses markers represent the experimental data of the master curve, and lines represent the fitting for each model. It is observed that the three models describe properly the relationship between the complex viscosity and the reduced frequency.

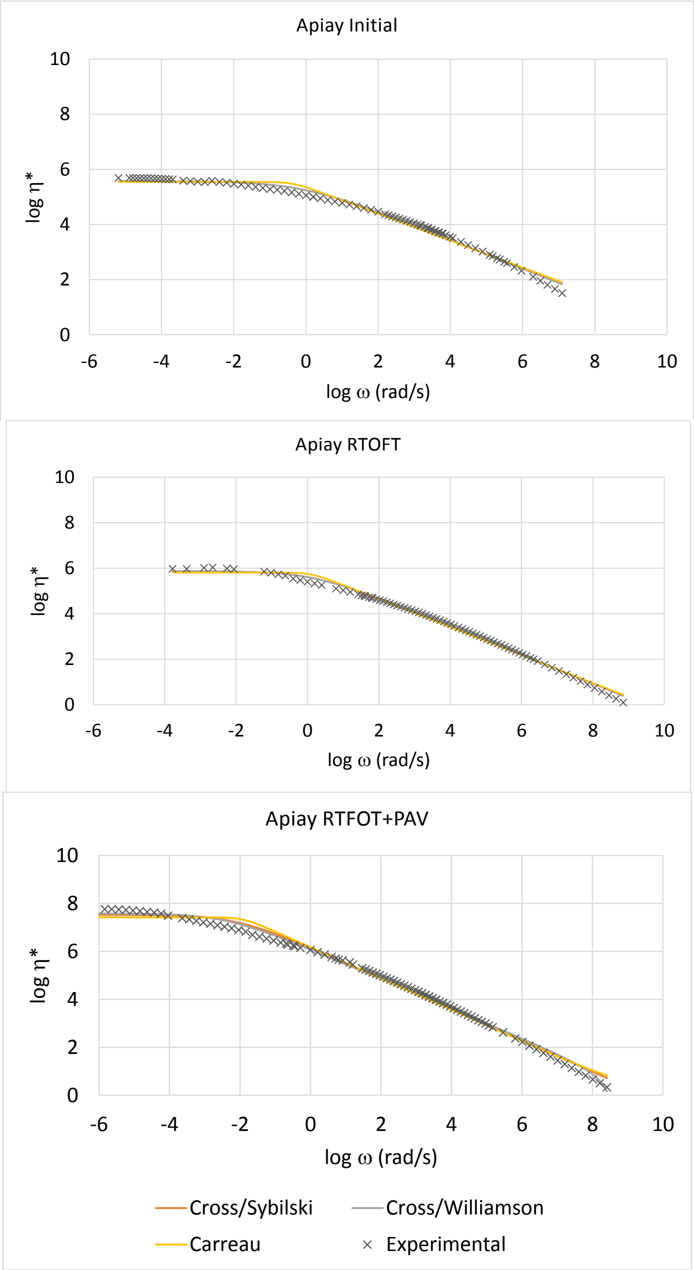

Figure 2: Complex viscosity master curves for Apiay bitumen in its initial (unaged), RTFOT and RTFOT+PAV aged condition, and their fitting for Carreau, Cross-Williamson and Cross-Sybilski models. (η* in Pa·s).

Figures 3 and 4 show the fitting for Barrancabermeja and Boscan bitumen respectively.

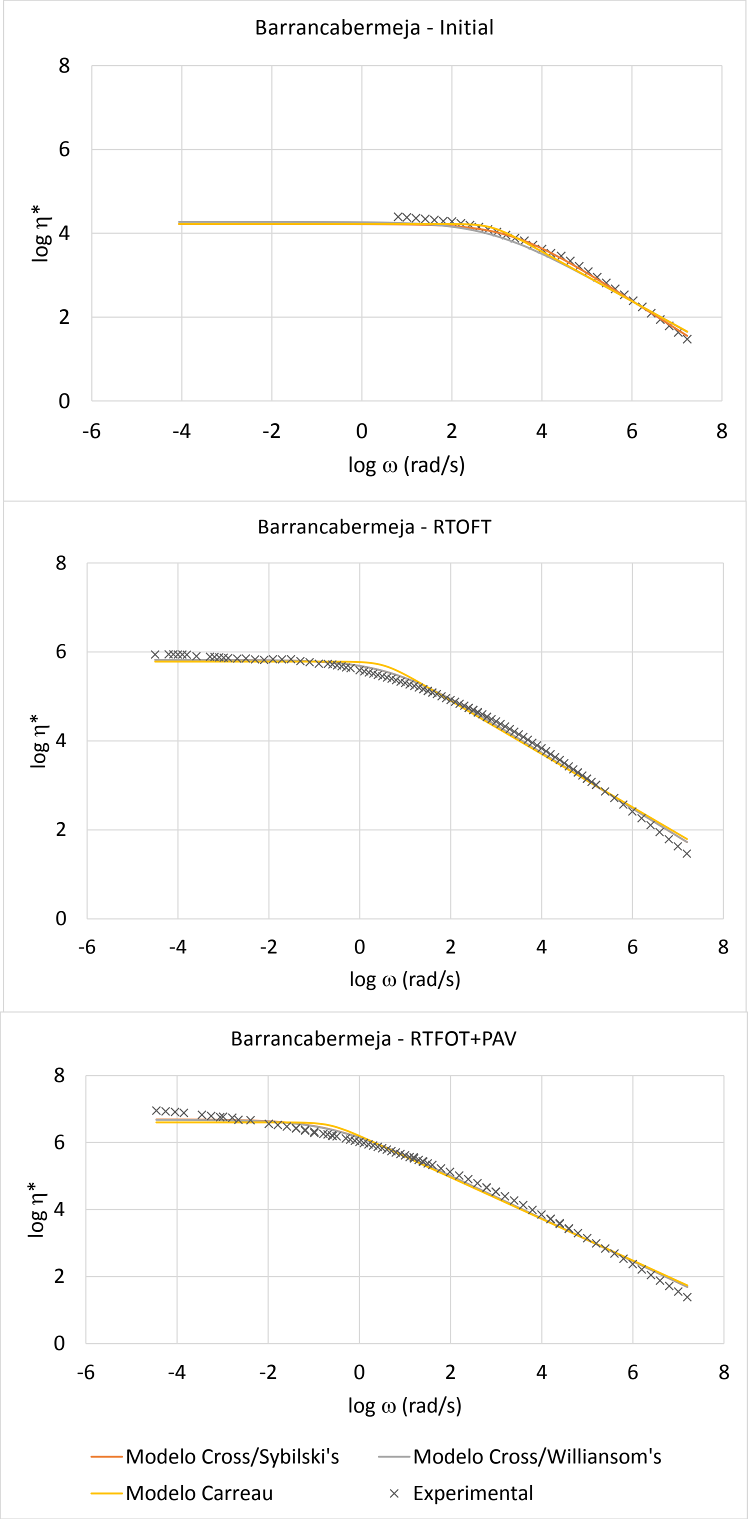

Figure 3: Complex viscosity master curves for Barrancabermeja bitumen in its initial (unaged), RTFOT and RTFOT+PAV aged condition, and their fitting for Carreau, Cross-Williamson and Cross-Sybilski models. (η* in Pa·s).

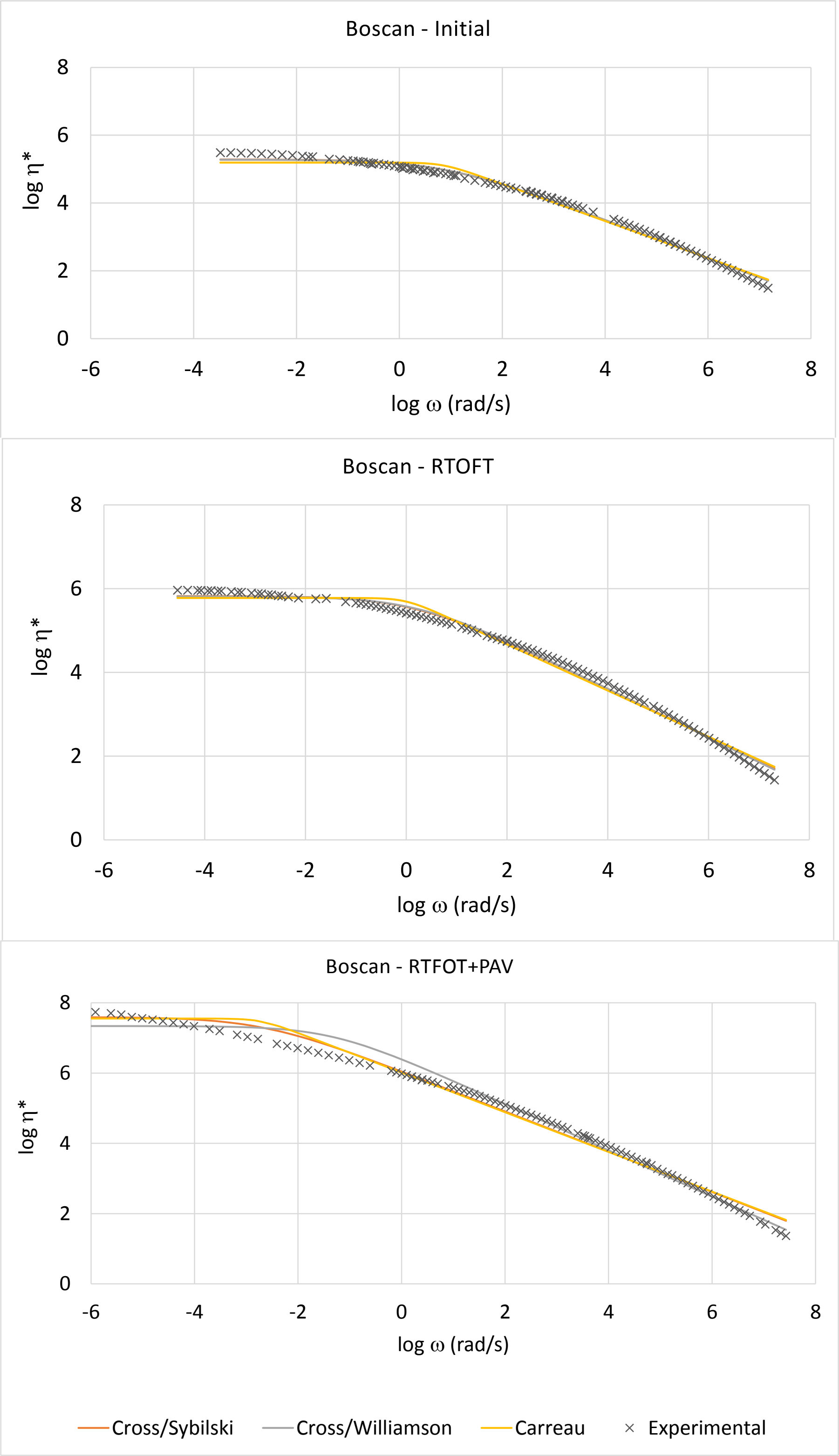

Figure 4: Complex viscosity master curves for Boscan bitumen in its initial (unaged), RTFOT and RTFOT+PAV aged condition, and their fitting for Carreau, Cross-Williamson and Cross-Sybilski models. (η* in Pa·s).

From Figures 2, 3 and 4 it is observed that the models provide a valid prediction for the relationship between the complex viscosity and the reduced frequency. Table 1 shows the parameters for each model (obtained by least squares fitting), and the evolution of each parameter with the ageing level of bitumen. ZSV values are highlighted, and it is observed that this parameter depends on the source of the bitumen and the ageing level. Comparing the ZSV values for the three bitumen in their initial state, Apiay bitumen shows the highest ZSV value, followed by Boscan and Barrancabermeja bitumen. When considering the ZSV increasing on the short term ageing (RTFOT) and long term ageing (RTFOT+PAV), the Apiay bitumen shows the least changes, both in the short and long term. However, it must be considered that not only the consistency of a bitumen indicates about its quality, since there are chemical properties that contribute to their interaction with other materials. Apiay bitumen is known to have poor adhesion properties, affecting the service of pavements built with this bituminous binder. It has been shown in other studies that the chemical composition, together with the type and distribution of functional groups of bitumen affects their surface and adhesion properties. For the Apiay bitumen, even though there have been developments at the facility for mixing the crudes that are fed to that refinery, some compatibility drawbacks are evident when this bitumen (Apiay) is used in road building. Figure 5 shows the dependence of the ZSV with ageing level for each asphalt, and the value of ZSV obtained for each model. It is observed that the ZSV increases with ageing, then the resistance to permanent deformation increases as the asphalt ages, due to the rearranging of components under the action of loads.

Table 1: Zero shear viscosity and other parameters for Cross-Williamson, Cross-Sybilski and Carreau models, in bitumen (unaged, RTFOT and RTFOT+PAV aged samples), for a reference temperature of 25°C

	Apiay Initial			**Apiay RTFOT**			**Apiay RTFOT+PAV**		
Parameter	1	2	3	1	2	3	1	2	3
η_o	3,73E+5	3,75E+5	3,52E+5	7,5E+5	7,5E+5	6,49E+5	3,36E+7	3,81E+7	2,62E+7
η_∞	-	9,88E-2	9,65E-2	-	9,98E-4	8,05E-2	-	-6,13	1,87
K	1,249	1,270	2,285	0,763	0,763	0,784	131,338	261,946	81,553
M	0,52	0,52	0,49	0,63	0,63	0,62	0,65	0,62	0,65
	Barrancabermeja Initial			**Barrancabermeja RTFOT**			**Barrancabermeja RTFOT+PAV**		
Parámeter	1	2	3	1	2	3	1	2	3
η_o	1,67E+4	1,87E+4	1,68E+4	6,62E+5	6,63E+5	6,06E+5	4,88E+6	4,75E+6	3,99E+6
η_∞	-	9,96E-2	9,73E-2	-	1,00E-2	1,00E-3	-	1E-1	9,69E-2
K	4,53E-4	1,336E+3	1,286E+3	0,203	0,204	0,296	4,149	3,971	4,363
M	0,69	0,60	0,59	0,63	0,63	0,60	0,64	0,64	0,62
	Boscan Initial			**Boscan RTFOT**			**Boscan RTFOT+PAV**		
Parámetro	1	2	3	1	2	3	1	2	3
η_o	1,92E+5	1,9E+5	1,56E+5	6,65E+5	6,53E+5	6,01E+5	3,92E+7	2,18E+7	3,56E+7
η_∞	-	9,97E-2	9,83E-2	-	9,96E-2	9,68E-2	-	1,02E-1	1,12E-1
K	0,140	0,134	0,144	0,697	0,594	1,029	485,208	22,909	526,47
M	0,57	0,57	0,55	0,58	0,58	0,55	0,57	0,66	0,56

Columns with number 1 are for the Cross-Sybilski model, number 2 for the Cross-Williamson model and 3 for the Carreau model.

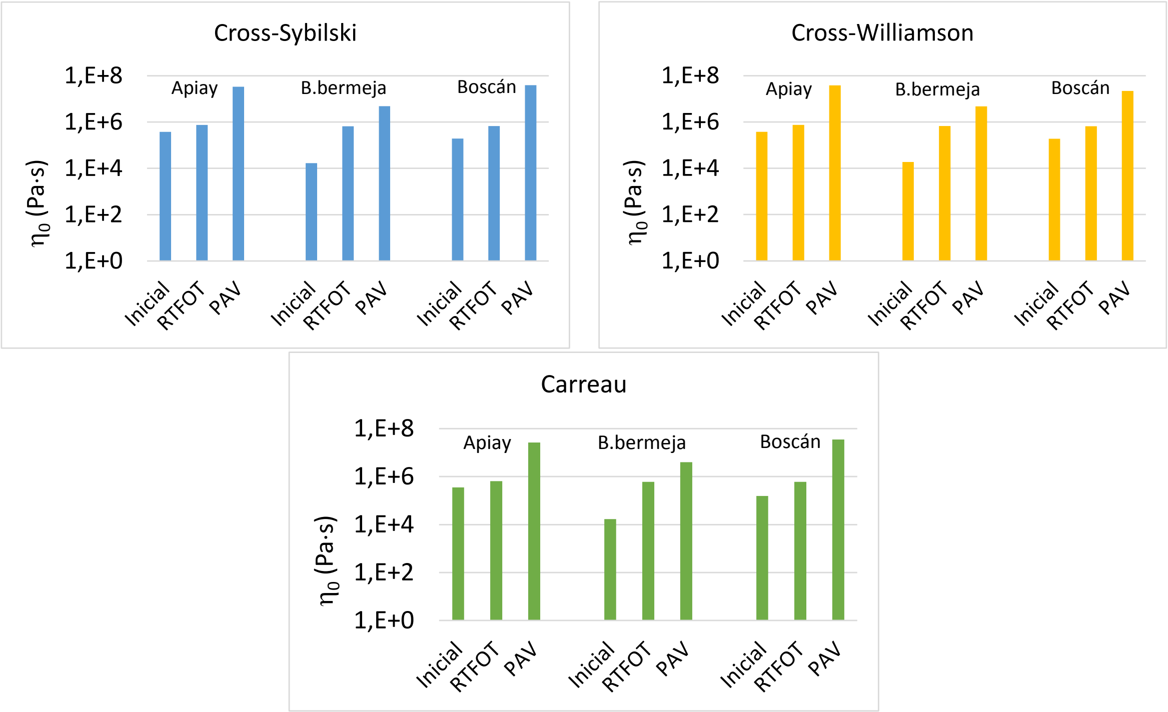

Figure 5: ZSV dependence with the bitumen source (Apiay, Barrancabermeja y Boscán) and the ageing level (unaged, RTFOT and RTFOT+PAV aged).

4. CONCLUSIONS

A least square fitting was used to determine different parameters in models proposed by Carreau, Cross-Sybilsky and Cross-Williamson, that describe the relationship between the complex shear viscosity and the oscillatory frequency. The main parameter from this study was the Zero Shear Viscosity (ZSV) and its evolution with the ageing level in three bitumen from different refineries. The three models provide a proper prediction of the parameters and, as expected, the ZSV increases with ageing level. Several factors affect the ZSV value obtained by the least square fitting, such as the type of test (in this case, the data were gathered by doing oscillatory tests on bitumen), the parameters used for the tests, and the software used for data fitting among others. When considering the ZSV in a practical application for bitumen, such as road building, it is desirable that the ZSV is high enough so the pavement does not rut during its initial service. It is also desirable that the ZSV does not increase significantly with ageing, since this indicates for the bitumen and pavement stability under traffic loads, as well as the capability of the bitumen to recover from traffic loads. According to this, Apiay bitumen would be the most appropriate material for road building, since its ZSV in the unaged condition is the highest and furthermore, the ZSV changes the least among the three bitumen studied. However, other studies have shown that the chemical distribution in Apiay bitumen causes incompatibility drawbacks, and makes it susceptible to the thermal and photo-oxidation, and in turn, to the chemical deterioration. Finally, for future works, it is necessary to obtain the ZSV at reference temperatures different from 25°C, in order to get a further insight of the behaviour of these bitumen at different locations where the mean temperatures are higher or lower than 25°C.

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