Life cycle of bitumen: ageing-regeneration-ageing

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ABSTRACT

Asphalt recycling is nowadays a requirement that accounts for demands on sustainability and energy efficiency. Despite being a minor component, the bitumen binder plays an important role in asphalt performance and also contributes for pavement deterioration. During its full lifetime bitumen faces different aging processes, mainly due to interactions with environment, which involve changes in chemical composition, in structure and microstructure and, by consequence, changes in rheological behavior (rheological material functions and material constants).

From the perspective of bitumen regeneration, there are some relevant aspects like: (1) To what extent is it possible revert the ageing of bitumen? (2) To what extent can regeneration processes restore original bitumen properties? (3) What kind of response can we expect from regenerated bitumen when facing a new ageing cycle? There is no single answer to these questions, since several factors are to be considered such as the degree of ageing of bitumen in RAP (Reclaimed Asphalt Pavement), the RAP content and the properties of the new binder added to RAP. The methodology used to evaluate bitumen properties is behind those answer, since it provides the tools for understanding the phenomena that are taking place.

The [ageing-regeneration-ageing] life cycle of bitumen used in Portuguese road construction was evaluated following a methodology based on chemical, structural and rheological characterization. Chemical analysis included the follow up of generic fractions (SARA, saturates+aromatics+ resins+asphaltenes) at different stages of the ageing and regeneration processes, as well as the pursuit of oxidation by infrared spectroscopic index. Structure and microstructure were assessed by using gel permeation chromatography (under extreme conditions) and atomic force microscopy. Furthermore, a rheological characterization was done, by measuring the relevant material functions in different regimes (dynamic and permanent (steady)).

Keywords: Ageing, Chemical properties, Reclaimed asphalt pavement (RAP) Recycling, Rheology

1. INTRODUCTION

Asphalt recycling is nowadays a requirement that accounts for demands on sustainability and energy efficiency. Despite being a minor component, bitumen plays an important role in asphalt performance and also contributes for pavement deterioration. During its full lifetime bitumen faces an ageing process, mainly due to interactions with environment, which involve changes in chemical composition, in structure and microstructure, and by consequence, changes in rheological behavior.

Hot asphalt recycling practices require the addition of softer bitumen, sometimes in the presence of additives (rejuvenators, softening agents…), in order to compensate the increase in hardness of the aged binder. The grade of the new binder to be added in Reclaimed Asphalt Pavement (RAP) formulation is usually determined by blending charts or equations such as log-pen rule.

If we want to go deeper in the knowledge of pavement recycling from a perspective of bitumen regeneration we must give emphasis to relevant aspects like: (1) To what extent is it possible to reverse the ageing of bitumen? (2) To what extent can regeneration processes restore original bitumen properties? (3) What kind of response can we expect from regenerated bitumen when facing a new ageing cycle? There is no single answer to any of these questions, since several factors are to be considered such as the degree of ageing of bitumen in RAP, the RAP content and the properties of the new binder added to RAP. The methodology used to evaluate bitumen properties is behind those answers, since it provides the tools for understanding the phenomena that are taking place.

We present here some results about a laboratory study of the life cycle of bitumens used in Portuguese road construction comprising the ageing-regeneration-ageing steps, with the primary objectives of understanding the influence of the degree of ageing of the bitumen (before regeneration), its percentage in the regenerated formulation (related to RAP content) and the influence of using different bitumen regenerators. The bitumen to be regenerated was artificially aged at specific conditions in order to obtain two ageing levels, a general purpose one and another much more severe. Taking in mind the higher levels of RAP content in use at present or considered as desirable target, we used 40% and 70% of aged bitumen in the formulation of regenerated binders.

The methodology to characterize the [ageing-regeneration-ageing] cycle of bitumen was based on an ensemble of chemical, structural and rheological properties. Chemical analysis included the follow up of generic fractions (SARA - saturates, aromatics resins and asphaltenes) at different stages of the ageing and regeneration processes, as well as the pursuit of oxygenated species using an infrared spectroscopic index. Structure and micro-structure were assessed by using gel permeation chromatography (HP-GPC), under extreme conditions, and atomic force microscopy (AFM). Furthermore, the rheological characterization of all bitumens considered was performed by measuring the relevant rheological material functions in different regimes (dynamic and permanent (steady)).

2. AGEING-REGENERATION-AGEING CYCLE

2.1 Ageing of bitumen (production of aged bitumen for regeneration) – First step of bitumen life cycle

In the present study, the aged bitumen for regeneration was produced at the laboratory (artificial ageing). The main reasons for performing artificial ageing stand on the possibility of control of the ageing process in a reproducible way and on the easy way of getting the required amounts of aged bitumen needed for the next steps of the cycle and for performing the characterization tests.

In the production of aged bitumen different aspects were considered:

1) Characteristics of the refinery (original) bitumen: A 35/50 grade bitumen was chosen, because it is one of the most used grades in Portuguese road construction.

2) Levels of ageing: Collected samples of aged bitumen extracted from RAP in Portuguese roads fall within two ranges of penetration (in 0,1 mm units): 15/20 and the 10/15 penetration ranges. Any of these ranges constitute the targets for the artificial ageing procedures. In the framework of European RAP practices [1], the value of (15 x 0,1) mm is considered as a boundary below which there are more requirements needed, including a more demanding selection of the binder.

3) Conditions of ageing: In general, bitumen ageing proceeds in two stages. The first one occurs during asphalt production, storage and laying (short-term ageing). The second stage includes the different ageing mechanisms during in-service life (long-term ageing). Ageing, is caused, in different proportions, either by changes in chemical composition of bitumen (due to oxidation, evaporation, exudation…) or by physical hardening. Major relevance has been given to oxidative ageing due to chemical reactions between oxygen and bitumen components.

Oxidative conditions (temperature, accessibility of oxygen, UV radiation, etc.) are not the same in short-term ageing and in long-term ageing, involving different reaction mechanisms. Distinct thermal oxidative ageing methods have been developed to simulate ageing such as: Rolling Thin-Film Oven Test RTFOT (EN 12607-1) for simulating short-term ageing; Pressure Ageing Vessel PAV (EN 14769) for simulating long-term ageing.

Since RTFOT conditioning is very much time consuming due to low yield, we replaced the sequence RTFOT+(PAV, 100ºC for 20 hours) by a single PAV ageing with modified conditions: 100ºC for 25 hours, designated herein as PAV25. This choice is based on the work of Migliori and Corté [2]. PAV25 ageing of the original 35/50 bitumen resulted in a decrease of the penetration to (17 x 0,1) mm, within the 15/20 penetration range considered above. For a more severe ageing simulation, in order to get harder bitumen, in the penetration range 10/15, the running time of PAV test was increased to 95 hours, maintaining the temperature at 100ºC – the ageing with these conditions is designated herein as PAV95. Figure 1 displays the evolution of the penetration (EN 1426) in PAV25 and PAV95 ageing.

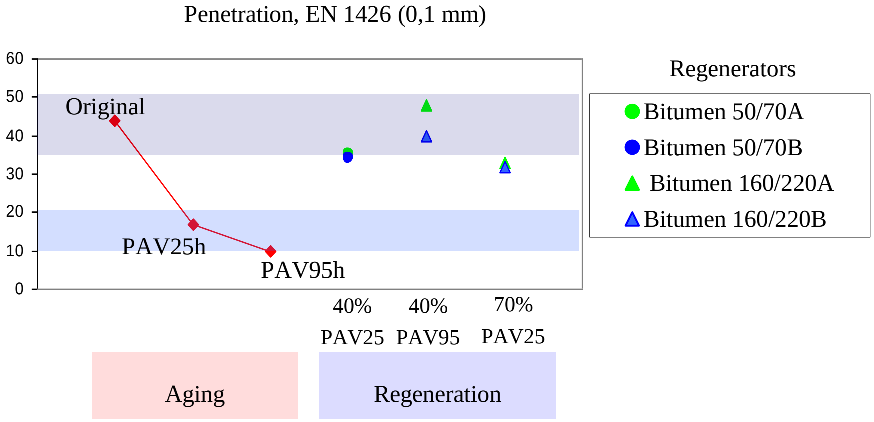


Figure 1 – Penetration of bitumens after ageing and regeneration processes

2.2 Regeneration of aged bitumen – Second step of bitumen life cycle

For the regeneration process, different penetration grade bitumens (50/70 and 160/220) were selected as regenerators. These binders differ in crude source and in refining conditions, providing different chemical compositions and structures (Table 1) and also different rheological properties (Figure 2). The formulation of regenerated bitumens took into account the following requirements:

- Use of the two different artificial aged bitumens (PAV25 and PAV95);
- Use of two aged bitumen contents: 40% of PAV25 or PAV95 aged bitumens; 70% of PAV25 aged bitumen;
- Production of 35/50 penetration grade regenerated bitumens.

Table 1 – Characteristics of bitumens used as regenerators

Bitumen grade	Refinery	Penetration EN 1426 (0,1mm)	SARA fractions				I_c	Agglomerates (%)
			Saturates (%)	Aromatics (%)	Resins (%)	C_7-Asphaltenes (%)		
50/70	A	55	3,1 ± 0,3	58,5 ± 1,6	28,8 ± 1,4	9,6	0,15	2,1
50/70	B	56	7,4 ± 0,7	48,7 ± 1,6	29,4 ± 1,8	14,5	0,28	8,0
160/220	A	169	3,3 ± 0,4	64,3 ± 0,9	25,4 ± 0,8	7,0	0,11	1,6
160/220	B	176	9,4 ± 0,7	52,6 ± 1,9	28,6 ± 1,6	9,4	0,23	4,2

Note: SARA fractions, I_C and agglomerates content are determined as described in chapter 3.

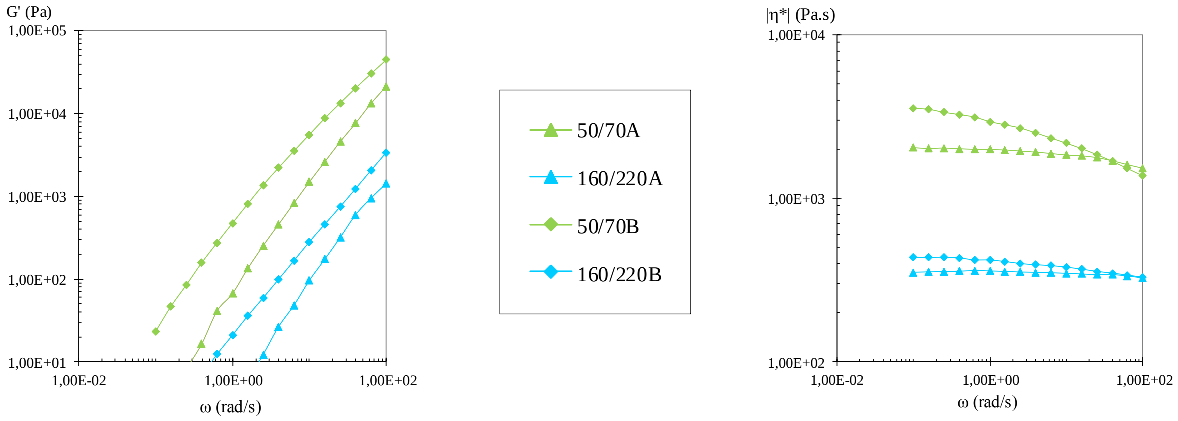


Figure 2 – Elastic modulus and complex viscosity, at 50ºC, of bitumens used as regenerators

Taking into consideration the above criteria, six regenerated bitumen formulations were produced (see Figure 3), with penetration values in the 35/50 range or slightly below (regenerated binders produced with 40% PAV95 aged bitumen have penetrations of (32 x 0,1) mm and (33 x 0,1) mm), as shown in Figure 1. It was obtained similar consistencies between the regenerated binders with 40% and 70% of PAV25 of aged bitumen, by adjusting the penetration grade, respectively, 50/70 and 160/220, of the bitumens used as regenerators. The comparison between regenerated binders with 70% PAV25 and 40% PAV95 holding the same regenerators (160/220) showed distinct values of penetration. It is detected a greater change in consistency by using 40% of the most aged bitumen (PAV95) then by using a much higher quantity (70%) of the less aged bitumen (PAV25).

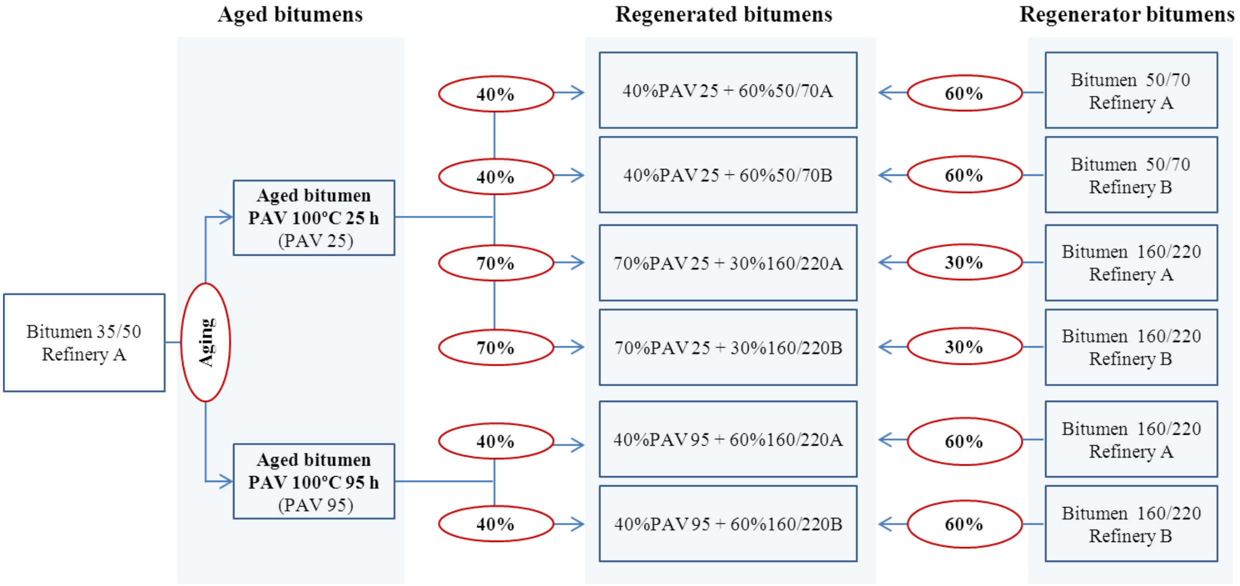


Figure 3 – Formulation of regenerated bitumens

2.3 Ageing of regenerated bitumen – Third step of bitumen life cycle

To complete the life cycle, a last step was considered: artificial ageing of regenerated bitumen. For this step, the currently specified full ageing sequence was considered, i.e., RTFOT (EN 12607-1) was followed by PAV ageing at 100ºC during 20h (EN 14769). This sequence is designated herein as (RTFOT+PAV20).
The virgin 35/50 grade (original) bitumen, used in the production of the aged bitumen for the regeneration process previously considered, was also aged following the RTFOT+PAV20 conditioning. Thus, it becomes possible a comparison of the effect of RTFOT+PAV20 ageing in the properties of both regenerated bitumen and refinery bitumen.

3. CHARACTERIZATION OF BITUMEN

3.1 Chemical characterization

Bitumens were separated into four generic fractions: saturates, aromatics, resins and asphaltenes (SARA fractions). Asphaltenes were precipitated with n-heptane, following the procedure of ASTM D 6560. The n-heptane soluble compouds constitute the maltenes fraction. A further analysis of maltenes by thin-layer chromatography provided separation of the other generic fractions (saturates, aromatics, resins).
Thin-layer chromatography with flame ionization detection (TLC-FID) was performed in Iatroscan MK6 analyzer (Iatron Laboratories Inc. Tokyo, Japan), using a procedure previously described [3]. Chromatographic separations were carried out on specially design silica coated quartz rods (Chromarod® - SIII). Maltenes solutions in dichloromethane were spotted on rods and a sequence of eluents allowed the separation of the various fractions: saturates, eluted with n-heptane; aromatics eluted with toluene/n-heptane (80/20 by volume); resins remaining in the spotted area. Chromatograms were recorded using Clarity Lite software developed by Data Apex.
Several reactions have been taken as responsible for the chemical transformations that occur in the ageing of bitumens [4-6]. Among them, there is the formation of functional groups containing oxygen, more particularly, sulfoxides and carbonyl, and the polyaromatization of naphthenic structures. However, in this paper only the presence of carbonyl groups, like ketones, acids or anhydrides [7], were considered, due to their important contribution to the polarity of molecules and hence to molecular associations [8].
Fourier transform infrared spectroscopy (FTIR) analysis was used to detect the absorption band of carbonyl groups, centered around 1690 cm^{-1}. The evolution of the amounts of carbonyl groups through the life cycle of bitumen was assessed by determination of the carbonyl index, defined as follows [8,9]:

$$\text{Carbonyl index, } I_{C=O} = I_{co} = A_{1690}/(A_{1460}+A_{1376}) \quad (1)$$

With: A_{1690} – C=O band area centered around 1690 cm^{-1}; A_{1460} – CH_2 band area centered around 1460 cm^{-1}; A_{1376} – CH_3 band area centered around 1376 cm^{-1}. The band areas were measured from valley to valley.
FTIR analysis were performed with a Nicolet Magna 550 spectrometer, in the transmission mode. Bitumen films were prepared on sodium chloride plates using a controlled temperature hot plate. The spectra were collected in the range

from 4000 cm^{-1} to 625 cm^{-1}, with a resolution of 4 cm^{-1}; each spectrum is an accumulation of 32 spectra. The spectra were analyzed using Omnic v6 software.

3.2 Structural characterization

Bitumen has been traditionally described as a colloidal system, with asphaltenes in the core of micelles [10]. Asphaltenes are peptized by resins, which are dispersed in an intermicellar environment constituted by aromatics and saturates. According with Yen interpretation of bitumen structure [11], not only asphaltenes molecules can associate, forming micelles, as well as micelles can agglomerate.

Taking into account the work developed by Brûlé et al. [12], an indirect assess of the colloidal structure was made by conducting high pressure gel permeation chromatography (HP-GPC) in extreme conditions of high sample concentration and high elution speed. Within those specific conditions, it is expected to access the colloidal profile, with a chromatographic separation of agglomerates of asphaltenes micelles, single asphatenes micelles and single molecules (intermicellar environment constituted by saturates and aromatics). HP-GPC was conducted in a Waters HPLC equipment, comprising an UV detector (set at $\lambda = 340$ nm). The chromatographic column was a Resipore, with a nominal particle size of 3 µm, from Polymer Laboratories. The mobile phase was tetrahydrofuran (THF), with a flow rate of 3 ml/min. Analyses were done with 3% (v/w) bitumen solutions prepared in THF; 10 µl of this solution were injected into the chromatographic system. Data acquisition was done by Empower 2 software provided by Waters. Analysis of the HP-GPC chromatograms allowed the determination of agglomerates content in bitumen.

Another approach to the characterisation of bitumen structure stands on the determination of colloidal instability index (Ic), introduced by Gaestel et al. [13], used to differentiate between "sol" and "gel" structures. I_C can be calculated from SARA fractions weigh content (χ_i):

$$I_c = (\chi_{asphaltenes} + \chi_{saturates}) / (\chi_{aromatics} + \chi_{resins})$$

The calculation of I_C was introduced in the study just as complement approach of bitumen structure, as it is surrounded by certain criticism because it doesn't render important factors contributing to thermodynamic equilibria, as, for example, peptizing power of resins and capacity of asphaltenes for being peptized by resins, i.e, of intermolecular interactions.

The microstructure of the surface of bitumen was characterized by atomic force microscopy (AFM), using a NanoScope 3D atomic force microscope, from Veeco/Digital Instruments, at ambient temperature and humidity. Etched silicon probes with a nominal tip radius < 10 nm, a nominal spring constant of 42 $N.m^{-1}$ and nominal free resonance frequency of 320 kHz, were used. Areas of 5x5 μm^2 up to 15x15 μm^2 were scanned in the tapping mode, and both topographical and phase difference (PDM) images were recorded. Darker features in topographic images correspond to valleys while in PDM images the colour is darker as the phase lag is smaller.

3.3 Rheological characterization

Rheological measurements were performed in a controlled stress rotational rheometer Bohlin Gemini 200 (Malvern), using the parallel plates fixture (20 mm diameter), at different temperatures. Temperature regulation was done by air convection in a closed chamber.

The experiments reported here are frequency sweeps in the linear viscoelastic regime (at low shear amplitude). The frequency range from 0,1 rad/s to 100 rad/s, at 50ºC. One relevant rheological material function measured is the complex shear modulus G(iω) or dynamic shear modulus, given by

$$G(i\omega) = G'(\omega) + i.G''(\omega)$$

where G'(ω) is the in-phase or elastic component of the complex shear modulus (sometimes called storage modulus) and G" (ω) is the 90º out-of-phase or dissipative component of the complex shear modulus, also called loss modulus. Another material function is the modulus of the complex viscosity

$$\left|\eta(i\omega)\right| = \left|\frac{G(i\omega)}{i\omega}\right| = \frac{1}{\omega}.\sqrt{[G'(\omega)]^2 + [G''(\omega)]^2}$$

In general, the |η| versus ω curve reproduces, to a good approximation, the (shear) viscosity versus shear rate curve. This is an empirical result known as the Cox-Merz relation [14]. We checked the validity of Cox-Metz relation in studied bitumen. The Cox-Merz rule is quite practical for an experimentalist: at high shear rates, centrifugal effects (e.g. drain off of the sample) are avoided; at low shear rates, time consuming measurements, thermal degradation, evaporation of volatiles, etc. are all strongly reduced.

We checked the validity of Cox-Metz relation in the studied bitumen.

The Cox-Merz relation [14] relates material functions for steady shear flow to dynamic material functions in linear viscoelastic regime; Laun´s rule [15] relates material functions in shear and in elongational flows; Gleissle mirror relationships [16] relate transient material functions (viscosity and 1st normal stress difference) to steady state shear material functions. All them share the same characteristic: they started as empirical rules, but later on their range of applicability was shown to be very large [17, 18]. This suggests that there may be something hidden behind the heuristic formulas. Renardy [19] demonstrated very generally that materials with a very broad spectrum of relaxation modes, and the simplest possible strain-dependent damping function obey rules like the Cox-Merz rule to within a constant factor. More recently, Jaishankar and McKinley [20] demonstrated that the validity range of the Cox-Merz rule and Gleiisle mirror relations hold in the framework of fractional K-BKZ constitutive equations with a Mittag-Leffler relaxation function. The validity of Cox-Merz rule in the framework of the constitutive equation of Dhole-Leyghe-Bailly-Keunings is also discussed in [21].

4. RESULTS AND DISCUSSION

4.1 Ageing and regeneration – First and second steps of bitumen life cycle

Oxidative ageing is caused by a set of chemical reactions that can result in formation of high polar groups in bitumen molecules; by consequence, there is an increase in asphaltenes content at expenses of other less polar fractions: aromatics and occasionally resins [4]. The ageing of the 35/50 refinery (original) bitumen proceeds with an increase of asphaltenes content (Figure 4), detecting an important role of ageing time in PAV. Also the content of functional groups containing oxygen, not detected in the original bitumen, increases with ageing time, resulting in more than doubling the carbonyl index (Figure 4). So, there is an outstanding difference between the PAV25 and PAV95 aged bitumen in terms of chemical composition.

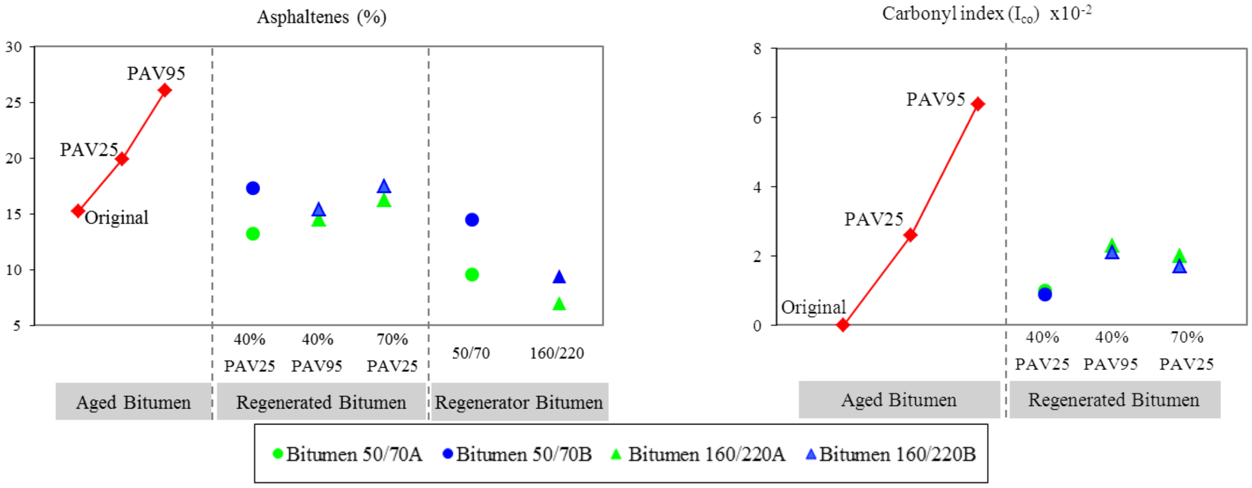


Figure 4 – Follow up of asphaltenes and carbonyl index during the ageing and regeneration steps of bitumen life cycle

Regeneration processes intend to reduce the effects of oxidative ageing by lowering the asphaltenes and carbonyl content (Figure 4). This is done by introduction of less-polar components in the aged bitumen. This sort of dilution effect was attained in all regenerated bitumens produced here. Some remarks are in order:

- Asphaltenes content in regenerated bitumen depends on the aged level (time of ageing in PAV), rate of aged bitumen and also on the composition of regenerators. The two regenerated binders with 40% of PAV25 aged bitumen had distinct asphaltenes content due to the marked differences in chemical composition of the two 50/70 bitumens used as regenerators (see Figure 4 and Table 1). The two other regenerators, 160/220 A and B (Table 1), have closest asphaltenes contents and cause similar changes in the regenerated binders produced in the same conditions (ageing time and aged bitumen content). By comparing the six regenerated systems (Figure 4), we found that the ones produced with 40% PAV25 define a range which contains all of the others, because of the composition of the used regenerators (Table 1). We can conclude that the composition of the regenerators can prevail over the time of ageing and aged bitumen content. The produced regenerated binders showed asphaltenes levels in the vicinity of the original 35/50 bitumen, demonstrating a “return” in composition with the regeneration process.
- Regenerators used here don’t show any detectable carbonyl functionalities, so they act almost exclusively as diluents. Regenerated binders are only differentiated by the aged bitumen. We find similarities between 40%PAV95 and 70%PAV25 regenerated binders, so there is a sort of equivalency between the effect of the longer PAV ageing time (95h) and of the higher aged bitumen content (70%) in terms of carbonyl index.

Topographic images from AFM surface analysis (Figure 5) revealed interesting features on bitumen microstructures. Comparing the four bitumen regenerators (50/70 from refinery A and B and 160/220 from refinery A and B), major differences were detected concerning the presence of catana- or bee-phase [22-25], recently attributed to crystals of paraffin waxes [26]. Bitumens from refinery A had smaller catanas as compared to the ones coming from refinery B. Harder grades also presented smaller catanas. By ordering these bitumens in terms of increase amount of catana-phase, 50/70A comes first, followed by 160/220A, third is 50/70B and the last is 160/220B. Looking at the images (Figure 5) of regenerated binders with 40% of PAV25 aged bitumen we also detect different microstructures according with the differences of regenerators binders. With the increase of the content of aged bitumen in regenerated systems (70% of PAV25), the regenerators fail to make so much difference in the final structure. These last structures are in between the ones of regenerated systems with 40%PAV25 in terms of catana-phase.

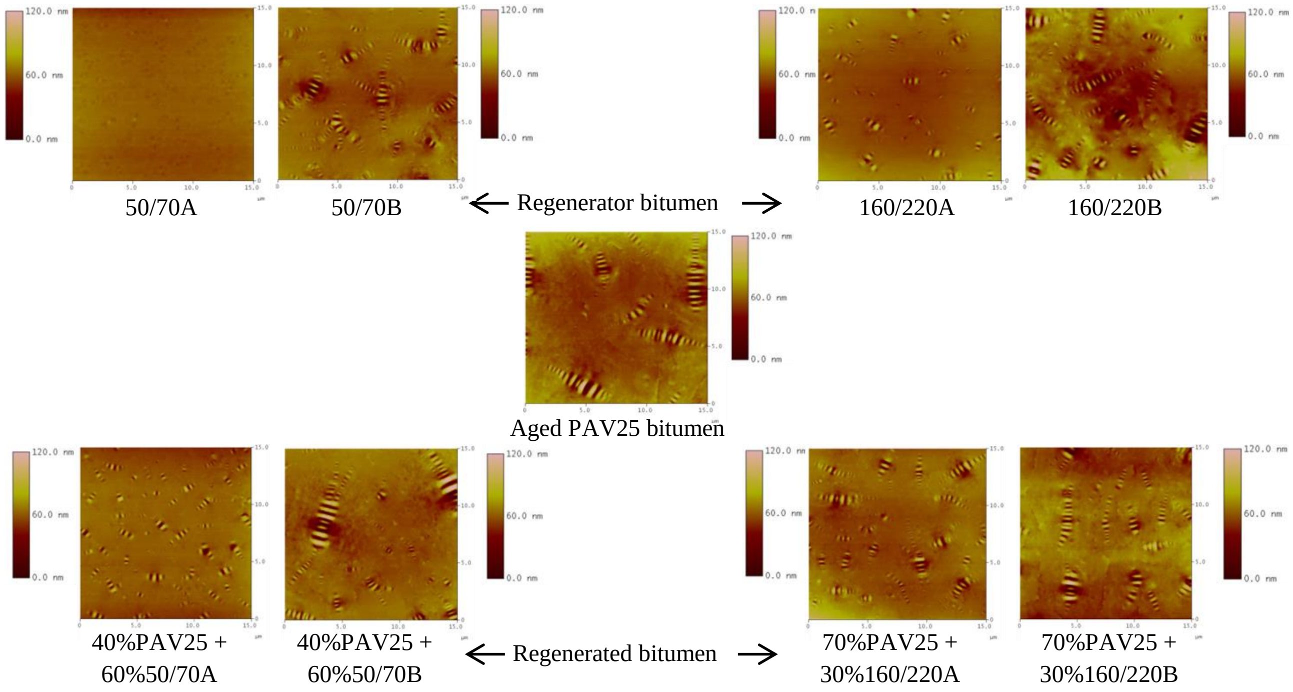


Figure 5 – AFM topography images of the regenerators, PAV25 aged bitumen and regenerated bitumens.

Quantification of the amount of asphaltenes agglomerates from HP-GPC analysis, following Brulê et al. [12], provides an indirect access to the structure. Data are indicative of reorganizations at structural level during ageing and regeneration processes, in order to attain new equilibria in regenerated systems (Figure 6). Agglomerates content increase with ageing, being sensitive to the time of conditioning in PAV (Figure 6). Regeneration yielded binders with lower contents under the influence of aged level and rate of aged bitumen and of regenerators. Produced regenerated binders have agglomerates content around the value of the original bitumen, used for ageing. The 40% PAV25 regenerated bitumens offer greater amplitude of values because of the more noticeable differences among the regenerators It was detected lower values in 40% PAV95 regenerated bitumens, compared with 70% PAV25 regenerated binders; so the content of regenerators prevailed over the degree of ageing of the aged bitumen in the setback of the ageing process.

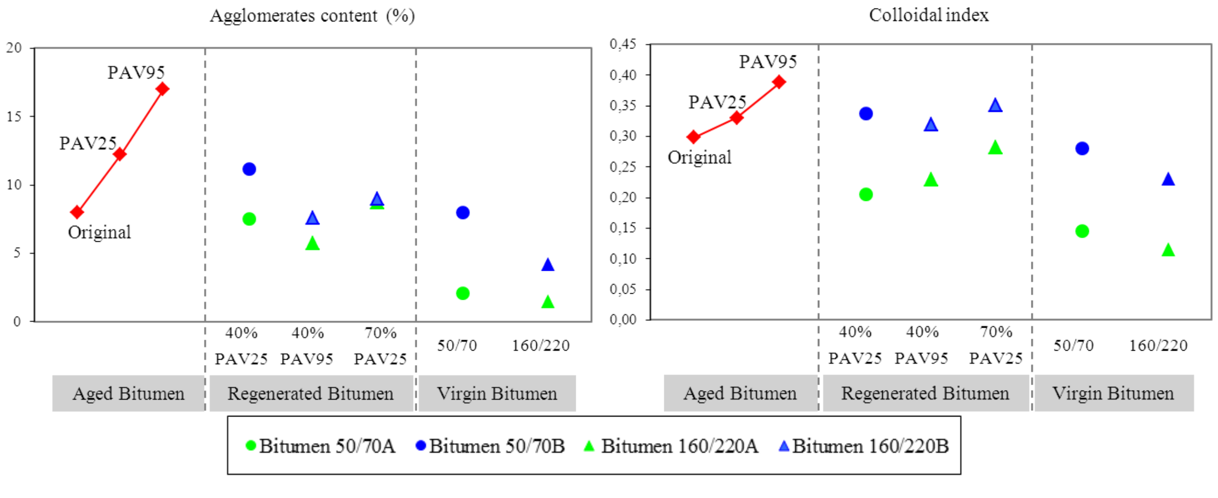


Figure 6 – Follow up of agglomerate content and colloidal index during the ageing and regeneration steps of bitumen life cycle

Colloidal index (I_c), based on SARA fractions (Figure 6), also confirms differences between regenerators coming from different refineries (Table 1 and Figure 6). Similarly to what happens with agglomerates content, bitumens from refinery A have a trend of lower I_c values compared to the ones from refinery B. A tendency is also detected for lower I_c of softer binders, within the bitumen from the same refinery. Ageing affects the balance of SARA fractions with a gradual rise of I_c from 0,30 to 0,39. Regenerated binders are influenced by the regenerator used, with the ones produced from refinery A regenerators having lower levels comparing with their congeners from refinery B, independently of the aged bitumen and its amount.

The curves representing the frequency dependence of the elastic shear modulus and complex viscosity at 50ºC, for the original bitumen (before ageing), aged bitumen (PAV25 and PAV95), regenerators and regenerated bitumens are presented in Figure 7 and Figure 8. As expected, ageing enhances both the elastic modulus and the complex viscosity; the effect is dependent on the time of ageing. On the contrary, regeneration induced changes in materials functions in the opposite sense to the ageing process; for most of the regenerated bitumens, the curves of complex viscosity or shear modulus versus frequency stay above the ones of the 35/50 original refinery bitumen and below the curves of PAV25 aged bitumen. The amount of decrease of elastic modulus and complex viscosity depends on the bitumen selected as regenerator, on the amount of regenerator used and also on the intensity of ageing (PAV25 or PAV 95).

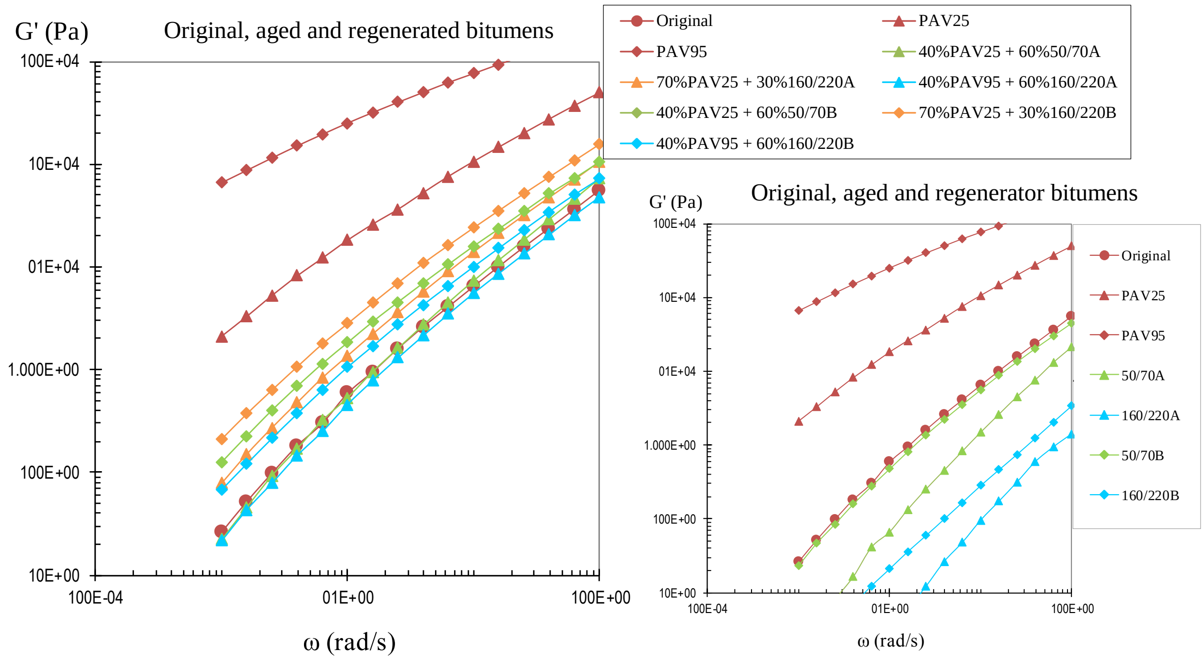


Figure 7 - Elastic modulus, at 50ºC, of aged, regenerator and regenerated bitumens

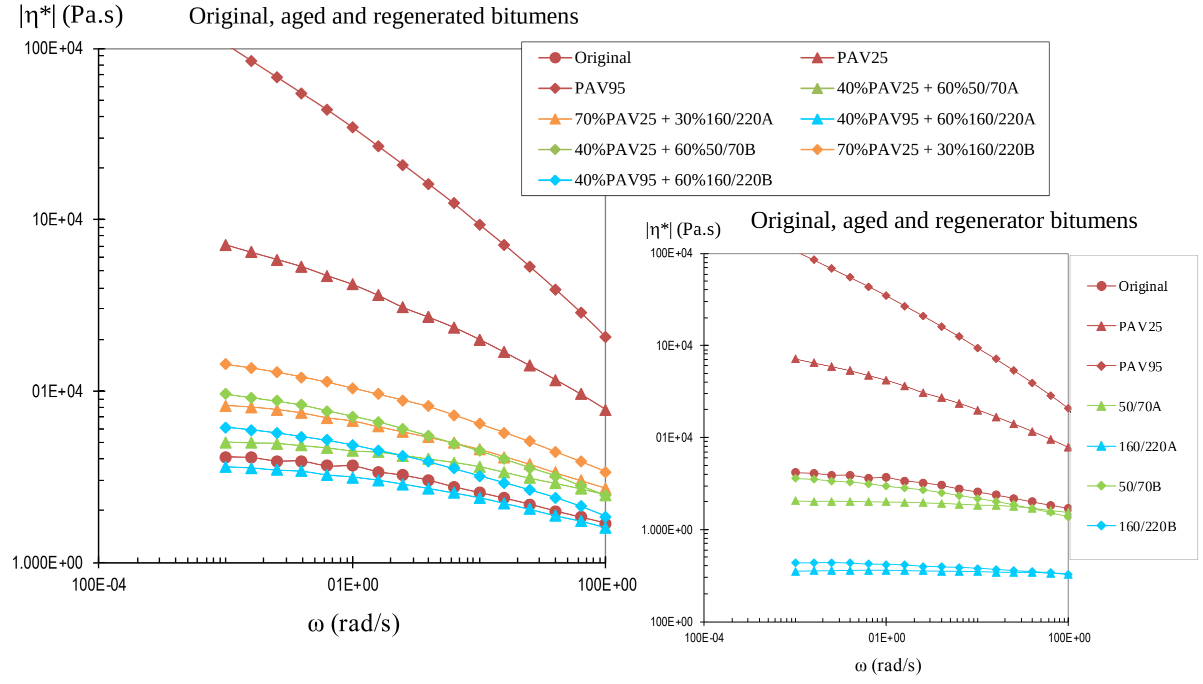


Figure 8 - Complex viscosity, at 50ºC, of aged, regenerator and regenerated bitumens

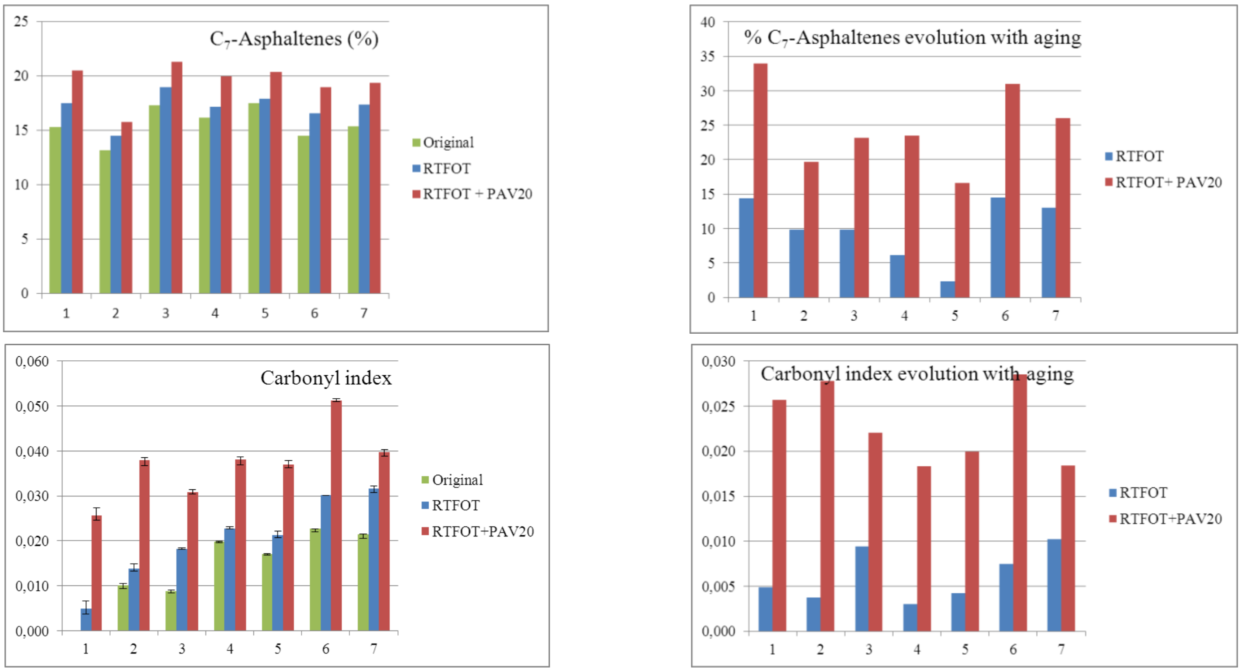
A more detailed analysis of the rheological experimental data (Figure 7 and Figure 8) leads to the following results:

- Regenerated bitumens produced using regenerators from refinery B have higher elastic modulus and complex viscosity values as compared to the one produced with regenerators from refinery A, which is in accordance with the rheological behavior of the regenerators.
- Comparing regenerated binders produced with the same 160/200 refinery bitumen, i.e., regenerated systems with 40% of PAV95 aged bitumen and 70% of PAV25 aged bitumen, we found that the first ones present lower elastic modulus and complex viscosity values. In that way, the use of smaller amount of the most aged binder (PAV95) has stronger effect in the decrease of rheological material functions as compared to the one of higher amount of the less aged bitumen (PAV25); in other words, the degree of ageing superseded the aged bitumen content.
- For the regenerated 40%PAV25 bitumens produced using 50/70 penetration grade, both the elastic modulus and complex viscosity stay between the values of the other two regenerated systems. This result puts emphasis on the importance of the combination of multiple variables in the resulting properties of the final product.

4.2 Ageing – Third step of bitumen life cycle

To complete the life cycle study, a last step was taken, corresponding to the ageing of the regenerated binders and also of the 35/50 grade refinery bitumen by the currently specified full ageing sequence of RTFOT followed by PAV20. The results from chemical and structural characterization after ageing are presented, respectively, in the bar charts of Figure 9 and Figure 10.

As expected, there is a rise in asphaltenes content during the ageing process (Figure 9), confirming the existence of oxidative transformations which result in an increase of the polarity of the bitumen components. The rise seems to be gradual; the evolution after PAV ageing tends to be at least of the same magnitude of the raise after RTFOT. If we can notice a trend with RTFOT ageing (70%PAV25 regenerated binders offer more ageing resistance, followed by 40%PAV25 and then by 40%PAV95), it is lost after ageing in PAV, keeping up only the less ageing resistance of 40%PAV95 regenerated bitumens. The 35/50 grade refinery bitumen joins the group of the binders with the higher levels of asphaltenes increase after both ageing.



1. Bitumen 35/50
2. Bitumen 40%PAV25 + 60%50/70A
3. Bitumen 40%PAV25 + 60%50/70B
6. Bitumen 40%PAV95 + 60%160/220A
7. Bitumen 40%PAV95 + 60%160/220B
4. Bitumen 70%PAV25 + 30%160/220A
5. Bitumen 70%PAV25 + 30%160/220A

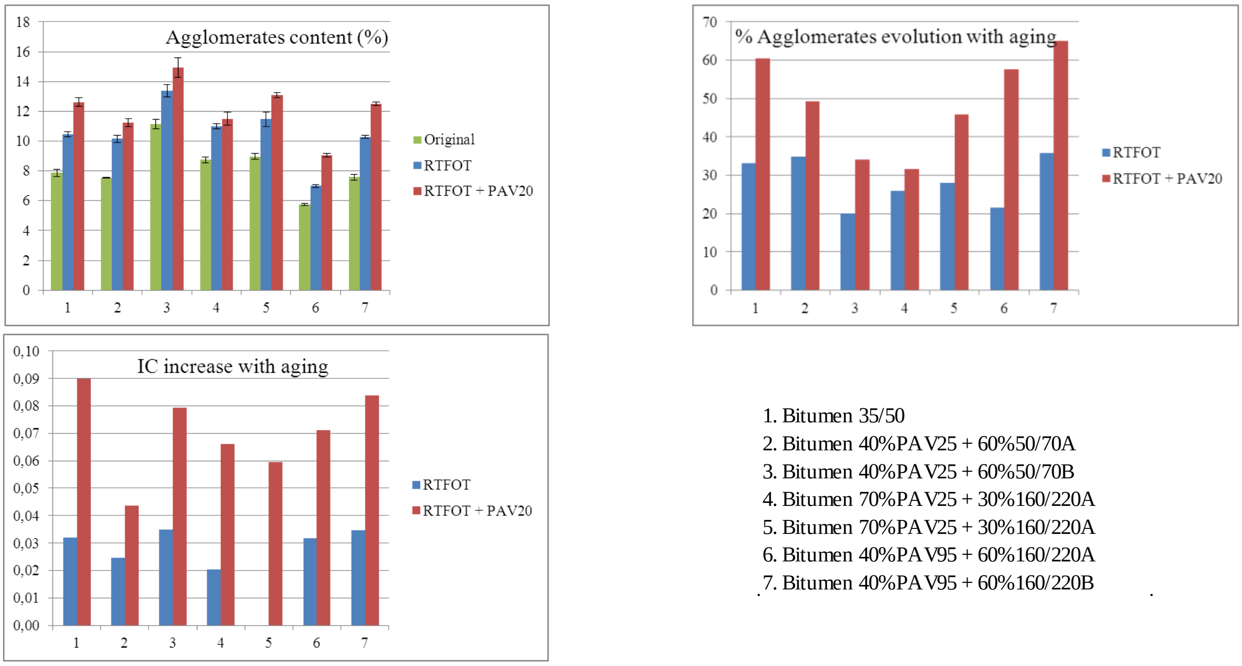
Figure 9 – Results of the chemical characterization after RTFOT followed by PAV20 ageing

The bitumen oxidation increased the amount of carbonyl functions. It is detected a sharply increase after PAV20 ageing when compared to the evolution after RTFOT (Figure 9). No correlation was found between the evolution of carbonyl index and the origin of regenerated binders (aged level and rate of aged bitumen and composition of regenerator). The 35/50 refinery bitumen is the only one that shows no detectable carbonyl groups before ageing and it is also the one with the lower carbonyl index after any of the ageing procedures. However, once more, this bitumen stays in the group of the less resistance to ageing with regard to formation of carbonyl groups, i.e., more susceptible to oxidation.

Ageing is also characterized by an increase in the content of agglomerates of asphaltenes micelles, as shown in Figure 10.

Different kinds of behaviour may be considered as relates to the content of agglomerates (Figure 10) :

- For some regenerated bitumens, RTFOT is the ageing conditioning procedure that causes a bigger increase in the agglomerates content. This is the case for 40%PAV25 and 70%PAV25 regenerated binders.
- For the other regenerated bitumens (40%PAV95), PAV20 is the ageing procedure that induces greater changes in agglomerates content.
- For the 35/50 grade refinery bitumen, RTFOT and PAV20 have similar effects in the increase of agglomerates content.

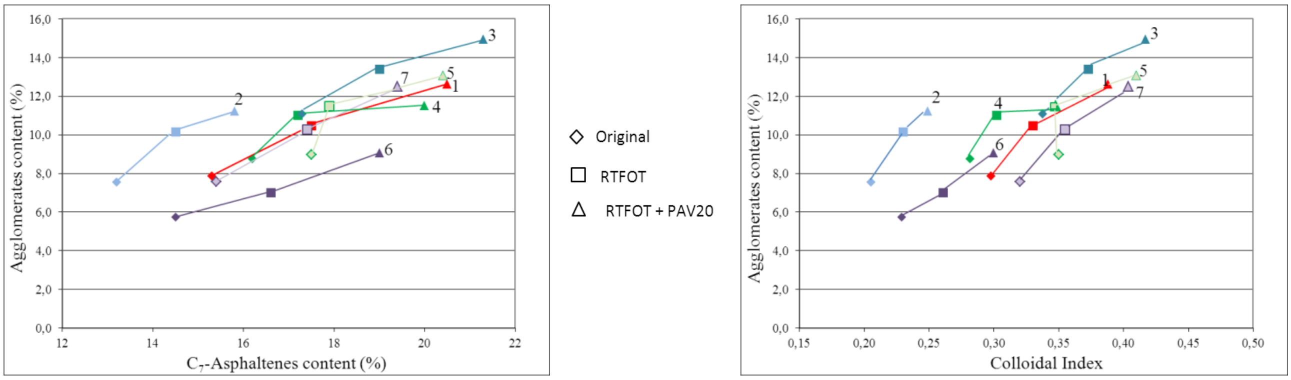


1. Bitumen 35/50
2. Bitumen 40%PAV25 + 60%50/70A
3. Bitumen 40%PAV25 + 60%50/70B
4. Bitumen 70%PAV25 + 30%160/220A
5. Bitumen 70%PAV25 + 30%160/220A
6. Bitumen 40%PAV95 + 60%160/220A
7. Bitumen 40%PAV95 + 60%160/220B

Figure 10 – Results of the structural characterization after RTFOT followed by PAV20 ageing

The evolution of the agglomerates content with ageing reveals a 35/50 grade refinery bitumen within the most susceptible binders to age, joining the group of the 40%PAV95 regenerated systems.

Agglomerates formation may be correlated with asphaltenes content and, hypothetically, with colloidal index [8]. Those data related to the seven bitumens considered in this study were plotted in Figure 11. There is a general trend to an increase in agglomerates content with the rise of asphaltenes content and of colloidal index. However, no rule could be established with the plotted data.



1. Bitumen 35/50
2. Bitumen 40%PAV25 + 60%50/70A
3. Bitumen 40%PAV25 + 60%50/70B
4. Bitumen 70%PAV25 + 30%160/220A
5. Bitumen 70%PAV25 + 30%160/220A
6. Bitumen 40%PAV95 + 60%160/220A
7. Bitumen 40%PAV95 + 60%160/220B

Figure 11 – Comparison between asphaltenes and agglomerates content and between colloidal index and agglomerates content of bitumens before and after ageing

Figure 12 shows the comparison between the evolution in carbonyl index and in agglomerates content of the seven bitumens after RTFOT and PAV20 ageing. From the collected data it is possible to detect two distinct ranges: one range for the RTFOT data, with lower values of carbonyl and agglomerate evolutions; other range for the PAV data, with higher values of carbonyl and agglomerate evolutions.

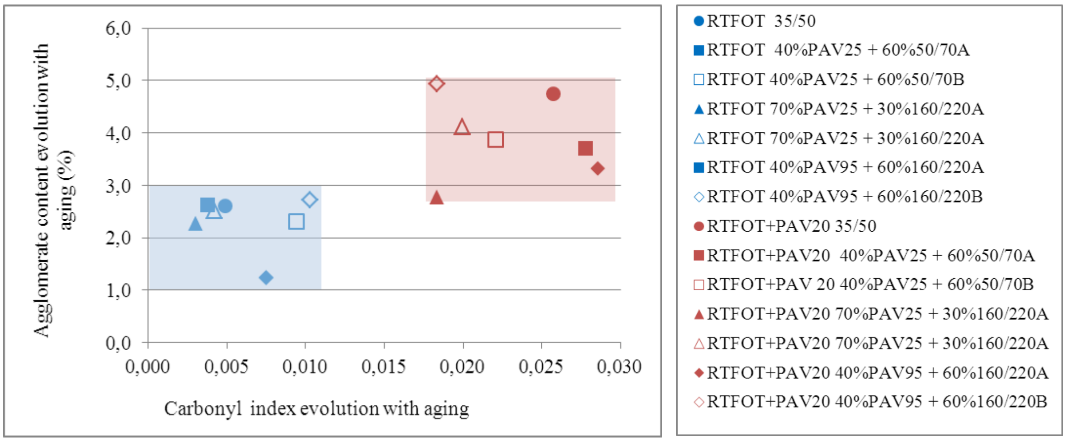


Figure 12 - Comparison of the evolution in carbonyl index and in agglomerates content of bitumens after ageing

Both elastic modulus and complex viscosity of regenerated bitumen increased with the amount of ageing (Figure 13). Nevertheless, generally, there are no changes in the relative order of the corresponding curves before ageing (Figure 7 and Figure 8). Therefore, regenerated bitumens produced with regenerators from refinery B keep higher elastic modulus and complex viscosity values as compared to their corresponding pairs where regenerators from refinery A were used. Also, regenerated systems with 70% of PAV25 aged bitumen keep higher elastic modulus and complex viscosity values as compared to the regenerated ones of lower aged bitumen content, i.e., 40% of PAV95 aged bitumen.

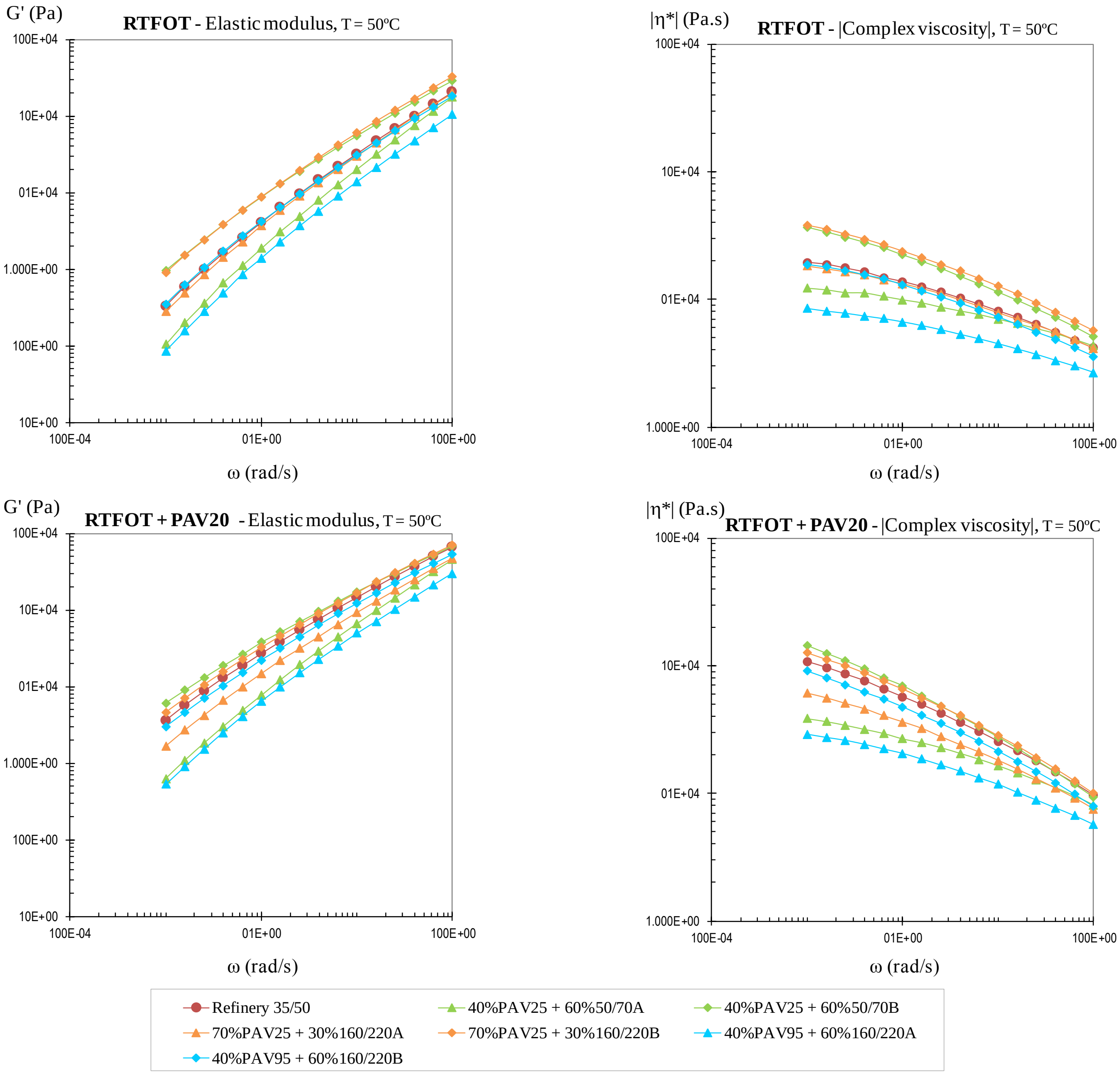


Figure 13 - Elastic modulus and complex viscosity, at 50ºC, after RTFOT and RTFOT+PAV20 ageing

Ageing changed, however, elastic modulus and complex viscosity of the virgin 35/50 bitumen relatively to regenerated binders; if, before ageing, this bitumen was within the binders with lower values of elastic modulus and complex viscosity, after RTFOT and PAV20, it happens to be in the middle of regenerated binders. Thus, we can conclude that the virgin 35/50 bitumen has a trend to be less resistance to ageing than the regenerated produced with regenerator binders from refinery A, with a more marked lag for the 40%PAV25 and 40%PAV95 systems.

5. CONCLUSIONS

Production of regenerated bitumens by mixing artificial aged bitumens with refinery binders (regenerators) led to “new” systems with their own identity in terms of chemical, structural and rheological properties. These new equilibria resulted from the balance of several variables: the ageing history (PAV25 or PAV95) of the aged bitumen; the nature of bitumen regenerator, in terms of crude source and refining process; the relative quantity of aged and regenerator binders in the mixture (40% or 70% of aged bitumen).

For most of the properties considered here, changes due to regeneration occurred in opposite direction to the ones during ageing. From chemical characterization, it was detected a decrease in asphaltenes content and in carbonyl index caused by dilution effects arising from the mixture with regenerators. The indirect access to the structure by determination of the HP-GPC population content correlated to the agglomerates of asphaltenes micelles also revealed an opposite movement towards the decrease of agglomerated species, as could be expected by a dilution effect. Rheological material functions - elastic modulus and complex viscosity - also decrease with regeneration. AFM topographic images from bitumen surface revealed changes in microstructure, namely in the shape of catenae and amount of catana-phase, indicating a structural reorganization during regeneration.

Regenerator bitumens play an important role in the regeneration process. Chemical, structural and rheological properties of regenerators can outweigh the influence of time of ageing and content of aged bitumen in regenerated systems. A strong dependence of the regression of the ageing effects is observed: the asphaltenes content decreases, as well as the agglomerates content and the colloidal index. Rheological material functions, such as the storage modulus and the modulus of the complex viscosity, also present a strong dependence of the amount of regenerator used (curves look approximately equidistant in a log scale).

Analysing, more particularly, the combine influence of the extent of ageing and the content of the aged bitumen in the regenerated system, i.e., the regenerated bitumens with 40% PAV95 and 70% PAV25 aged bitumen, using the same regenerators, it was found a more pronounced decrease in properties (asphaltenes content, agglomerates content, elastic modulus and complex viscosity) with the first ones. So, the use of less quantity of a higher aged level binder had much more impact in changing properties in the regeneration process than the use of a higher quantity of the less aged bitumen, in other words, the degree of ageing superseded the aged bitumen content.

The last step of bitumen life cycle, involving the ageing cycle RTFOT and PAV20 of regenerated and refinery bitumens, brought the following conclusions:

- The influence of RTFOT and PAV20 ageing depends on the selected property. For instance, PAV20 induced a sharp increase in carbonyl index, however, a quite similar effect in asphaltenes content could be detected when compared with RTFOT. The increase in agglomerates content was more pronounced after RTFOT for certain bitumen and after PAV 20 for the others binders.
- Regenerated systems progressed differently depending on the analysed property. Yet, among them, it can be pointed out the 40% PAV95 regenerated binders as they had the highest increase in asphaltenes and agglomerates content. However, in terms of rheological properties the 40% PAV95 regenerated binders maintain after ageing lower values of elastic modulus and complex viscosity.
- The refinery 35/50 bitumen was less resistance to ageing when compared with the majority of regenerated systems, in terms of chemical and structural properties. In terms of rheological properties, values of elastic modulus and complex viscosity progress to a higher level than several of the regenerated binders.

Finally, it was shown that the regeneration process can produce bitumens with chemical, structural and rheological properties close enough to the ones of a refinery bitumen. Nevertheless, regenerated bitumen includes a significant amount of oxidized bitumen components, the effect of which is attenuated due to the increase in the maltenes content brought by the regenerator. In any case, regeneration of bitumen is a process that depends on the chosen regenerator and on the amount of ageing and the composition of the aged bitumen.

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