Temperature Effect of Asphalt Production on the Thermo-Chemical Properties Of Kraft Lignin

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Abstract: Global warming has triggered a series of strategies and efforts to reduce greenhouse gas emissions and increase the reuse and recycling into asphalt pavements. One of these, is the reduction of production temperatures of asphalt mixtures, and the other is using sustainable antioxidants, such as Kraft lignin, with high phenolic content. Kraft lignin is usually mixed at high temperatures without considering the effect of temperature on its antioxidant properties. This research aimed to study the impact of the production temperatures of asphalt mixtures on the thermo-chemical properties of Kraft lignin and its antioxidant capacity. To evaluate these properties, thermogravimetry, infrared spectroscopy, and DPPH tests were done. To validate the results, bitumen-lignin blends were prepared considering representative temperatures for Hot-Mix-Asphalt (HMA), 160°C, and for Warm-Mix-Asphalt (WMA), 135°C. Bitumen-lignin blends were prepared considering 0% and 20% Kraft lignin by total weight bitumen. The blended samples, unaged and aged. were evaluated considering mechanical, rheological, and chemical properties. The main conclusion of the study demonstrated that although Kraft lignin can be used in HMA, using it in mixtures with lower temperatures conserve its properties. WMA production temperatures preserve Kraft lignin's chemical properties, increasing the durability and resilience of bitumen throughout its service life.

Keywords: Kraft lignin, Bitumen, Asphalt Mixture, Thermogravimetric Analysis, DPPH, FTIR Analysis

1. Introduction

In recent decades, a growing awareness of the repercussions of global warming and climate change has underscored the urgent need to integrate environmentally friendly and sustainability-oriented approaches into development. In 2015, the United Nations approved the "2030 Agenda for Sustainable Development" with 17 goals. Goal N°13, "Action for the climate," seeks, in concordance with the Paris Climate Agreement (2015), to carry out activities that help to keep the increase in the average global temperature during subsequent years to remain below 1.5 Celsius degrees compared to pre-industrial levels (Ridoutt, 2021). To achieve this goal, various efforts have been developed by many types of industries (U.S. Department of Transportation, 2016). Most of these initiatives can be clustered as implementing strategies to reduce greenhouse gas emissions (GHGE), reusing different types of waste from various industries, and recycling several materials. These activities or actions have been incorporated into a relatively new concept called "Circular Economy" (Papamichael, et al., 2023). In this context, "Sustainable Transport Infrastructure" has been developed (Oltean-Dumbrava, et al., 2013), aiming to incorporate eco-friendly construction processes that mitigate environmental impact, GHGE, and energy consumption, while promoting increased reuse and recycling of various materials.

Asphalt mixture composites are blends of bitumen, a viscous liquid obtained from the oil refinery, with aggregates. Asphalt mixtures play a crucial role in infrastructure, thus constituting a fundamental and strategic component of the economies in most developed and developing countries. Approximately 95% of the road network in most countries has been built using asphalt as the primary material (Asphalt Institute, 2007) (Huang, 2004). Hence, researchers and practitioners have been making significant efforts to address

challenges associated with asphalt pavements, especially the variability in asphalt costs (Baek & Ashuri, 2019) (Whiteley, et al., 2005) (Qiao, 2019), limited availability of construction materials (Victory, 2022) (Hettiarachchi, et al., 2019), and adjustments to environmental regulations (Santos , et al., 2017). Thus, most efforts have been focused on enhancing bitumen characteristics to improve its performance. As part of these efforts, production techniques have been adapted with a significant change involving the adjustment of temperatures in the production of asphalt mixtures (Cheraghian, et al., 2020). According to their operational temperatures (Figure 1), asphalt mixtures can be classified into traditional or Hot Mix Asphalt (HMA) (150 – 180°C), Warm Mix Asphalt (WMA) (100 – 150°C), Half Warm Mix Asphalt (HWMA) (40 – 100°C), and Cold Mix Asphalt (0 to 40°C); HMA is the predominant and most widely chosen asphalt mixture globally (Rubio, et al., 2012) (EAPA, 2014). However, due to its production temperatures, this type of asphalt mixture is not considered environmentally friendly because it generates a large amount of GHGE and a large energy demand, making it necessary to use significant amounts of natural resources.

Furthermore, from a technical perspective, it has been demonstrated that HMA production causes bitumen aging due to oxidation processes (TRB, 2009) (Tauste, et al., 2018). This aging process mainly results from the mixing and compaction stages, where the bitumen is exposed to high temperatures during its construction stage (i.e., short-term aging), and throughout its lifetime (i.e., long-term aging), where asphalt layers are exposed to ultraviolet radiation (i.e., UV), high temperature, and other environmental effects. Aging changes the viscoelastic properties of bitumen, reducing its flexibility and making it more brittle, inducing cracking and failure. One possibility to mitigate the short-term aging effect is the construction of asphalt pavements using WMA, characterized by production

temperatures 20 to 30°C lower than for HMA. WMA offers advantages over HMA, for example, it diminishes bitumen oxidation and premature aging, enhancing its durability (Safaei, et al., 2014). From an environmental perspective, WMA reduces fuel and energy consumption, lowers GHGE, and minimizes the overall carbon footprint of the asphalt mixture (Padilha Thives & Ghisi, 2017).

Another strategy to mitigate the bitumen aging processes uses antioxidant additives, which have become a relevant alternative in producing asphalt mixtures (Sirin, et al., 2018). For example, Kasem et al. (Kasem, et al., 2019) conducted a detailed analysis of various commercial additives, including rejuvenators and antioxidant alternatives, most of them associated with synthesized materials. For this reason, these new types of modifying materials must meet the following requirements: compatibility with bitumen, improved performance and durability, minimal or no increase in the cost of the final product, and recyclability (Gaudenzi, et al., 2023).

In this context, lignin, one of the planet's most abundant biopolymers, and a primary component of plant cell walls, has gained increasing relevance as a bitumen additive (Buranov & Mazza, 2008). Its favourable binding characteristics promising rheological outcomes and positive impact on sustainability make it an appealing and environmentally friendly alternative. Lignin is available worldwide in copious quantities, with worldwide estimates of over 50 million tons produced yearly as a byproduct of the paper industry. Lignin is generally considered an industrial waste, and 98% of its total production is used as a fuel to generate electricity. Only 2% is recovered and used for other purposes, specifically as a natural antioxidant (Bajwa, et al., 2019).

Depending on the extraction method employed, there are four primary types of lignin: Kraft, Sulfonate, Soda, and Organosolv (Faruk & Sain, 2016) (Gellerstedt &

Henriksson, 2008). Among these lignin variants, Kraft lignin is the most widely and commercially available accessible forms, and Kraft and Sulfonated are the most used types of lignin in pavement engineering (Yao, et al., 2022). (Zhang, et al., 2021).

Researchers have analysed the antioxidant properties of Kraft lignin (Lu, et al., 2022), demonstrating that it can be used as a neutralizer, inhibitor, scavenger, or stabilizer of free radicals derived from oxidation processes. This final characteristic is possible because of the presence of diverse functional groups that contain oxygen (methoxy, aldehydes, carbonyl, and carboxyl groups) but mainly because of its high phenolic content that plays an important role toward lignin's antioxidant properties. This scavenging capacity of phenols is primarily attributed to the ability of the hydroxyl group to donate an electron to the free radical, effectively reducing its reactivity. The delocalized electrons in the aromatic ring of phenols also contribute to their antioxidant potential by assisting in the distribution of the unpaired electron from the free radical, further reducing its reactivity (Ortiz, et al., 2020).

The use of Kraft lignin started in the 1980s (Terrel, 1980) and has recently been identified for various applications in conventional asphalt mixtures and pavement engineering in general (Gaudenzi, et al., 2023) (Yao, et al., 2022) (Jedrzejczak, et al., 2021). Researchers have used Kraft lignin as a bitumen performance modifier, a partial substitute for bitumen, and a bitumen expander agent, improving its construction workability (Yao, et al., 2022). According to the literature, Kraft lignin improves the rheological properties of bitumen in both short-term and long-term pavement performance. It reduces aging associated with oxidation, one of the primary sources of cracking in asphalt pavements (Pan, 2012) (Xu, et al., 2017) (Zhang, et al., 2020) (Ren, et al., 2021). Previous research also indicates that mechanical agitation is the most common way to add

Kraft lignin into bitumen (Gaudenzi, et al., 2023) (Rezazad Gohari, et al., 2023). To achieve a homogeneous blend, bitumen is heated to 150°C-180°C to reduce its viscosity, and then the lignin is added at the same temperature to avoid thermal shock between the materials. Later, Kraft lignin and bitumen are mixed for approximately 40 to 60 minutes at 6000 rpm.

In conclusion, the literature review indicates a lack of standard procedures for bitumen modification with lignin. Additionally, the potential effect of asphalt mixture temperatures on the reduction of the antioxidant properties of Kraft lignin and its physical properties has not been studied under an experimental approach that includes different controlled blending test conditions.

This study aims to analyse the impact of conditioning temperature during the bitumen modification (bitumen-lignin blending) on the chemical and thermal properties of Kraft lignin and to investigate whether this conditioning reduces its antioxidant capacity. Thus, this research developed an experimental plan that begins by identifying the effect of asphalt mixture production temperatures on lignin. For example, for an HMA, the typical mixing temperature is 160°C; hence, the chemical and thermal characteristics of lignin were raised to this temperature without considering the impact over its properties. In addition, mechanical characterization of unaged and aged bitumen-lignin (i.e., physical and fundamental engineering properties) was carried out. The results of this study will enable bitumen science to define an optimal mixing temperature for the modification of bitumen with lignin and to reduce the potential adverse effect of temperature on its antioxidant properties.

2. Materials and test methods

2.1. Materials

2.1.1. Kraft Lignin

University Bio-Bio in Chile provided the Kraft lignin used for this study. This brownish powder lignin (Figure 2) was obtained as a paper and pulp industry byproduct. The analysis of elemental components - Carbon, Hydrogen, Nitrogen, Sulphur, and Oxygen (determined by the difference of subtracting the sum of the other elements from 100%revealed that this sample of Kraft lignin comprised 98% Carbon, Oxygen, and Hydrogen. Additionally, the lignin sample contained a 1.4% Sulphur content resulting from the Kraft process used to obtain this type of lignin (Table 1). Another significant element, as previously explained, is the phenolic content, which is crucial for lignin's antioxidant properties. The CHNS analysis was conducted using an elemental determinator (LECO CHN 628 and 628 S). Moisture and Ash content were determined according to the UNE-EN 14774-2 and UNE-EN 14775 standards, respectively. Total Phenolic determination was carried out using the Folin-Ciocalteu method (Blainski, et al., 2013). This method is a colorimetric assay which measured the blue color intensity produced when phenolic compounds reduce the Folin-Ciocalteu agent under alkaline conditions. The calibration curve or standard was established with Catechol (methyl 11,12-dihydroxyabietate-8,11,13-trien-18-oate, MDTO). The quantification of the phenolic content was established by comparing the sample's absorbance to the calibrated curve of Catechol and the results are expressed as gr of Catechol equivalent per Kg of sample.

Morphological characterization was carried out with a Particle Size Distribution (PSD) Test to perform a dimensional analysis of Kraft lignin. This test was executed with a

laser diffraction technique using a Malvern Mastersizer 2000 equipped with a Hydro EV dispersion unit, and the liquid base was isopropyl alcohol instead of water to control for the hydrophilic behaviour of lignin. The measurement considered a range of 0.1 – 1000 µm to ensure a complete size distribution. The PSD test results, presented in Figure 3, of the powder lignin show that the maximum particle size (D100) was 105 µm, the nominal maximum size (D90) was 90 µm, the middle size (D50) was 42 µm; the most frequent particle size was 60 µm. In Figure 3, the red line represents the volume of the particle size, and the blue line indicates the accumulation of the PSD.

As part of the morphological analysis and for verification purposes, a Scanning Electron Microscope (SEM) - FEI Quanta FEG 250 was used to visualize the dimensions of lignin particles. The results obtained can be seen in Figure 4. Images of the measurements on different lignin particles (in green) are presented, confirming that the average size is approximately 60 microns. Finally, solubility analyses were conducted in both water and oil, revealing that Kraft lignin is insoluble in water and exhibits an affinity with oily bases. However, it is important to note that this characteristic was not considered in the present study.

2.1.2. Bitumen

The bitumen used in this study was a conventional type supplied by “Constructora Asfalcura SpA”, an asphalt company in Santiago, Chile. The characterization of this material is presented in Table 2, with results conforming to a CA-24 based on the Chilean viscosity specification (Ministerio de Obras Públicas de Chile, 2022). The bitumen grade was PG (64-22).

2.2. Test Methods

2.2.1. Thermal Characterization of Lignin

Thermal properties of Kraft lignin were obtained using a Thermogravimetric Analysis (TGA). This method measures the changes in weight of a sample as a result of increasing temperature at a constant heating rate and in a specific type of atmosphere (Air or Nitrogen). During the test, TGA typically samples suffer a degradation process, losing weight as a result of changes in their structural composition and reactions with their substances.

For the lignin characterization, this research used a Q600 SDT TA Instrument. Kraft lignin powder samples (20 ± 0,5 mg) were analysed under air atmosphere, and the testing temperature considered a range from 60 to 300°C, according to the usual production temperatures of asphalt mixtures, plus an extra 100°C. The heating rate was 10°C/min and the gas flow was 50 mL/min.

2.2.2. Chemical Characterization of Kraft lignin

Chemical properties of Kraft lignin were obtained using Fourier Transform Infrared (FTIR) Spectroscopy using a Shimadzu IRSpirit FTIR spectrophotometer. In this case, the method used to measure lignin was a transmission technique. The wavenumber ranged from 500 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. Forty (40) scans were recorded for each spectrum. Prior to each test, a background spectrum was captured, and a KBr pellet with Kraft lignin was prepared. To assess the consistency of the results, one replicate was considered per each sample.

2.2.3. Characterization of the radical scavenging activity of lignin

The characterization of the radical scavenging activity of lignin, as mentioned a relevant property associated with its antioxidant performance was evaluated using the The DPPH ((2,2-Diphenyl-1-picrylhydrazyl) test (Dizhbite, et al., 2004). This test is based on the reduction of the DPPH radical, a stable free radical with a deep violet color, to a yellow-colored upon reaction with an antioxidant. The degree of color change is measured spectrophotometrically providing a quantifiable indicator of the sample's antioxidant capacity.

To execute the test, approximately 1 gr of lignin was weighed and dissolved in 10 mL of methanol, then agitated in a shaker for 30 minutes. The supernatant was separated, and the sample was washed twice more with 10 mL of methanol. Each sample was prepared in triplicate.

The DPPH analysis was conducted in a 96-well microplate, with 22 µL of the sample mixed with 200 µL of DPPH radical at a concentration of 200 µM. Similarly, 22 µL of the sample was mixed with 200 µL of methanol as a blank. The mixture was incubated in the dark for 30 minutes and read at 520 nm. Results were expressed in µmol per gram of dry sample, based on a Trolox calibration curve with a linear range of 100 to 800 µM.

2.2.4. Bitumen Characterization

The characterization of the bitumen provided the identification of both physical and mechanical properties. The experimental plan for the physical characterization of bitumen included: 1) the penetration test, 2) the softening point test, and 3) the determination of rotational viscosity used to assess viscosity of bitumen at high temperatures, ranging from

60 to 200°C. In this specific case the viscosity was determined at 135 and 160°C. In terms of the fundamental properties, Rheological properties were determined using a Dynamic Shear Rheometer (DSR) - Discovery HR 20 TA instruments. This procedure assesses the shear complex modulus (|G*|) and the phase angle (δ). These two parameters indicate bitumen resistance to specific deformation and load and are very important in evaluating performance criteria across different stages of bitumen lifetime.

To assess the performance of bitumen mixed with Kraft lignin (bitumen-lignin), the tests outlined in Table 3 were conducted following Chilean specifications (Ministerio de Obras Públicas de Chile, 2022).

The chemical characterization of bitumen-lignin samples was conducted using the same methodology for evaluating Kraft lignin, the FTIR analysis. Due to bitumen's dark-colored nature, a single-point Attenuated Total Reflectance (ATR) fixture was used to obtain spectral data. According to the literature, to evaluate the contribution of Kraft lignin as an antioxidant material to bitumen, the analysis was focused on two specific functional groups: Carbonyls (C=0, ~1700 cm^{-1}) and Sulfoxides (S=0, ~1030 cm^{-1}) (Xu, et al., 2017) (Arafat, et al., 2019) (Zhang, et al., 2019) (Nie, et al., 2021). The main reasons to use these indicators are their direct relationship with aging and the chemical oxidation of the organic compounds in bitumen. An increase in these functional groups implies changes in the mechanical properties of bitumen, such as elasticity, and a reduction of its durability over its lifetime (Hofko, et al., 2017) (Xu, et al., 2017) (Nie, et al., 2021).

2.3. Kraft lignin Thermal Conditioning

To fulfil the research objective to examine the impact of temperature on Kraft lignin properties, samples were conditioned following the outlined procedures:

- For thermal characterization, six (06) lignin samples were stored in an oven at 60°C for 1 hour. This procedure, aimed at preventing agglomeration due to the hydrophilic behaviour of lignin, maintained the integrity of the samples. It is important to clarify that given the nature of the TGA test, these samples did not receive the conditioning scheme at different temperatures.
- For chemical characterization, samples of Kraft lignin were conditioned at different temperatures (i.e., 25, 80, 100, 135, 150, 180 and 200°C) with each sample exposed to its respective temperature level for 1 hour. Each temperature represented the average manufacturing temperature of the various asphalt mixtures (HMA, WMA, HWMA, and Cold mixture). Additionally, in particular, 25 and 200°C were considered for evaluating an initial condition as a reference point and to study an extra temperature effect over the typical range. Figure 5 shows the results of this sample preparation. There was a clear and pronounced alteration in the sample color, particularly when comparing the samples exposed to 25 and 200°C.

2.4. Bitumen–lignin samples preparation

To assess the performance of bitumen modified with the incorporation of Kraft lignin, mixing samples were formulated at two representative production temperatures: 160°C and 135°C to simulate HMA and WMA, respectively. Two levels of lignin content were considered: the first, serving as the baseline, with 0% lignin, and the second, with 20% lignin by total weight of bitumen. The selection of this specific percentage of lignin was based on bibliographic references and previous experimental experiences. This amount of lignin allows bitumen replacement without changing the specifications of base bitumen used in this research. (Marquez, et al., 2023).Studying these proportions clearly assess

lignin's effectiveness as an antioxidant agent.

Considering the hydrophilic nature of lignin, initial sieving was conducted before mixing to eliminate lumps, and the material was maintained in a controlled environment at 60°C to stop moisture sorption from the air. Simultaneously, the bitumen was heated to achieve the necessary fluidity for mixing; then, the lignin was gradually poured. The mixing process was conducted with a high-shear mixer for 45 min at 6000 rpm. The selection of this specific mixing parameters was based on literature review and previous experimental experiences done by the authors. With this mixing time and speed, it was possible to obtain uniform mixtures that allow us to continue with the following tests.

2.5. Short-term aging of bitumen-lignin samples

To study the antioxidant effect of lignin, this research focused on the period where bitumen undergoes its most significant oxidation which is associated with the stage of production and placement of asphalt mixtures. Bitumen-lignin blends was conditioned using the rolling thin film oven test (RTFOT). Each sample was poured into special glass bottles; meanwhile, the RTFOT was preheated to a standard temperature of 163°C for 2 hours. Then, the bottles containing bitumen-lignin were placed in a carousel inside the RTFOT, which rotated at 15 rpm. The aging time was 85 minutes, and the airflow rate was 4.0 l/min.

Figure 6 presents a photographic record of the bitumen modification process from the mixing procedure until the aging done with the RTFOT oven.

In summary, the bitumen preparation sample considered two (2) mixing temperatures, two (2) lignin content samples, and two (2) aging conditions for a total of 8 study cases. In each case, 6 samples were tested, leading to a total of 48 analyses.

3. Results and discussion

3.1. TGA - Thermogravimetric Analysis of Kraft Lignin

Figure 7 presents the results of the thermogravimetric tests. Grey curves depict the individual weight loss for each sample. The average weight loss is shown with the black curve, and the red curves show the upper and lower intervals (95% confidence). To analyse the variability, considering that lignin is a complex organic polymer, six samples were evaluated and were identified as LK T1 to LK T6. For ease of analysis, the initial weight of each lignin sample before TGA testing was normalized to 100%; consequently, the mass difference between the start of the test and the mass at different temperatures is expressed as a percentage on the vertical axis, ranging from 100% to 88%. As observed across the temperature range studied (60 to 300°C), the weight loss or degradation of lignin at the end of the test is slightly higher than 10%. Figure 7 shows that between the temperature range 140-160°C, the weight loss significantly increases. Between 60 and 140°C, the weight loss was 1.5%, while between 140 and 220°C, the weight loss was 2.5%. Above 220°C, the slope of the curve remains approximately constant. This situation shows that lignin undergoes chemical modifications when exposed to heating processes. The results are consistent with those of Brodin in 2009 (Brodin, 2009) and Haz et al. in 2019 (Ház, et al., 2019).

Figure 8 presents TGA results considering the production temperatures of the different studied asphalt mixtures. In the range of temperature corresponding to HWMA, the weight change is slightly appreciable, being less than 0.8 ± 0.4% when lignin is exposed up to 100°C. In the range associated with WMA, the weight variation can reach 1.7 ± 0.5 %

when the temperature is raised up to 150°C. Finally, for HMA, the value of weight lost can be more than 2.5 ± 0.5 % when the temperature reaches its maximum. Table 4 also describes the main results of the TGA analysis. In both Figure 8 and Table 4, the influence of the production temperature of each type of asphalt mixture is appreciable. As the temperature increases, Kraft lignin shows a gravimetric degradation, representing changes in its chemical structure. This transformation suggests potential implications for various properties and attributes of lignin, such as its antioxidant capacity.

The most significant impact is observed on Kraft lignin exposed to HMA temperatures, with a degradation (mass loss) of over 2%. This situation doubles the results obtained with WMA temperatures and triples them when compared with the mixing temperatures of HWMA. This situation indicates that, although using lignin with HMA is feasible, its effect would be more efficient when used in mixtures with lower production temperatures than HMA. The practical implications of this approach relate to the temperature control used by asphalt mixture manufacturers. They will improve and promote sustainability when they reduce asphalt mixture production temperatures, as explained in the introduction of this article, but they will also enhance the effectiveness of using Kraft lignin as a bitumen additive, optimizing its antioxidant properties.

The results of the Differential ThermoGravimetric (DTG) analysis are presented in Figure 9, for each analysed sample. Six samples were evaluated to examine material variability, with the grey curve indicating individual results. The black curve represents the DTG average of the six samples, and the red curve indicates the upper and lower intervals. The vertical axis is the variation in weight percentage over temperature, and the horizontal axis is the temperature range (60 to 300°C). The results reveal three distinct zones where Kraft lignin exhibits different behaviour. The first zone, within the range of 60-100°C,

displays high variability in the results, accompanied by a decrease in the slope of the curve. The second zone spans from 100 to 140°C, showing thermal stability in Kraft lignin performance and a notable reduction in measurement variability. Finally, the third zone, beyond 140°C, exhibits a consistent increase in slope throughout the temperature range associated with HMA. As shown in the range of temperatures studied, the differential analysis shows a wide variation, especially over 140°C, where the slope becomes more pronounced. This situation implies that the change in the lignin composition will become greater as the temperature increases. The findings from this analysis are congruent with those presented by Haz et al. in 2019.

Following the same procedure used to analyse the TGA curves, the results of the DTG analysis were compared with the production temperatures of different types of asphalt mixtures (Figure 10). In the range of HMA temperatures (150° to 180°C), the variation of the slope increases throughout the entire interval. This observation indicates that increasing the production temperatures induces continuous alterations in the chemical structure of Kraft lignin. The slope of the curve follows an opposite trend for HWMA. In the WMA temperature range, a thermally stable zone exists between 100 and 140°C, indicating no significant change in the characteristics of the lignin. The 105°C and 135°C temperatures show the most negligible impact on differential thermogravimetry. In summary, the DTG analysis, in alignment with the temperature ranges of the different asphalt mixture types, reveals a dynamic relationship between temperature and Kraft lignin properties.

3.2. FTIR Analysis of Kraft Lignin

Figure 11 shows the average FTIR results of each Kraft lignin sample exposed to different temperatures, according to the production temperature of various types of asphalt mixtures.

This figure illustrates the absorbance curves for each of the lignin-conditioned samples, where the black curve corresponds to the results of the lignin in its original condition (25° C for 1 hour), and the curve in red represents the lignin exposed to a temperature of 200°C, also for 1 hour. These two curves are considered boundaries of the experiment because both represent extreme situations found in the production and in-service conditions of asphalt mixtures, in particular the red curve (200°C) is related to very high mixing temperatures in asphalt mixture plants. The remaining curves represent the FTIR results of each sample tested at intermediate temperatures. The contrast between each absorbance curve reveals significant chemical alterations incurred by Kraft lignin due to exposure to conditioning temperature. The pronounced changes in the absorbance in the FTIR spectra indicate that the lignin molecules undergo substantive modifications. These transformations represent changes in chemical functional groups, intermolecular interactions, and structural rearrangements.

The results presented in Figure 12 demonstrate changes throughout the entire spectrum of the FTIR analysis. However, this article focuses specifically on the range associated with phenolic content. As previously explained, the phenolic content represents one of the most relevant properties that should make lignin considered a natural antioxidant. In this case, the spectrum of phenolic compounds, characterized by the stretching of the O-H bonds (OH functional group), is located between wavenumbers 3200 and 3600 cm-1. As shown in Figure 12, the phenolic content is significantly reduced when the samples are exposed to higher temperatures. When the boundary associated with the sample exposed to 200°C is analyzed, the phenolic content almost disappears. Figure 12 shows the variation of the phenolic content depending on the production temperatures, decreasing as the lignin conditioning temperature increases. When Kraft lignin is exposed

to temperatures associated with HWMA (between 40–100°C), the average phenolic content is 26%, for production temperatures of WMA (between 100–150°C) this average is 22%, and considering the HMA temperatures (between 150–180°C), the average content is approximately 10%. This analysis provides important insights into the temperature-dependent evolution of Kraft lignin phenolic properties, thus contributing to a comprehensive understanding of its potential as an antioxidant in asphalt mixtures. As the phenolic content is reduced, its ability to serve as a free radical scavenger or inhibitor is also reduced. These findings also indicate that the antioxidant attributes endure when lignin is exposed to HWMA and WMA mixing temperatures.

3.3. DPPH test – Assessment of the radical scavenging activity of lignin

The results of the DPPH test of each Kraft lignin sample, are presented in Figure 13. The vertical-axis represents the concentration of DPPH in µmol Trolox equivalents (TE) per gram (µmol/g), while the horizontal-axis shows the temperatures in degrees Celsius (°C) at which the lignin samples were processed.

The figure shows that there is a clear decreasing trend in the radical scavenging activity as the temperature increases from 25°C to 200°C. This suggests that higher processing temperatures reduce the antioxidant capacity of the lignin samples. Temperatures below 135°C, are more favorable for preserving lignin's antioxidant properties. Also the observed error shows a consistent results across replicates.

3.4. Results from bitumen-lignin blends characterization

3.4.1. Mechanical – Engineering Properties

Figures 14, 15, and 16 show the results of bitumen-lignin samples for the Penetration test,

Softening Point test and Penetration Index, respectively. Penetration test results (Figure 14) indicate that, as expected, the temperature used for modification (135°C or 160°C) hardens the bitumen. It is also important to highlight that the samples without lignin were more sensitive to temperature modification. This finding is notable for samples with 0% lignin: i) the samples exposed to 135°C decreased their penetration in 45% from their original condition to the RTFO aged state (6.56 mm to 3.64 mm), ii) the samples exposed to 160°C decreased their penetration in 38% (5.50 mm to 3.54 mm). Conversely, the bitumen-lignin samples (20% lignin content by weight relative to the bitumen) show lower penetration than the samples without lignin, regardless of the preparation temperature of the bitumen-lignin blend. The increase in the solid fraction of the bitumen explains this hardening. The effect of the RTFO in bitumen-lignin samples (20% lignin) prepared at 135°C was 32.89% (4.53 mm to 3.04 mm), and the samples prepared at 160°C, the RTFO effect was a reduction of 17.32% (3.54 mm to 2.93 mm). The antioxidant effect of lignin, i.e., the lower proportion of bitumen in the bitumen-lignin samples, explains these results.

Figure 15 shows the results obtained from the softening point tests. In contrast to penetration, by incorporating lignin into the bitumen, the softening point increases due to increased bitumen stiffness (demonstrated by the penetration results). The increase in the softening point in samples prepared at 135°C before and after RTFO was 5.83°C (11.32%) and 6.17°C (11.46%) for 0% and 20% lignin, respectively. For bitumen-lignin prepared at 160°C, the increase in softening point before and after RTFO was 4.67°C (8.98%) and 4.68°C (8.21%) for 0% and 20% lignin, respectively. Results show slight variation in the softening point in samples with lignin, indicating that results are inconclusive with regard to discerning the antioxidant effect of lignin or the lower proportion of bitumen in the bitumen-lignin.

Figure 16 shows the bitumen sensitivity to temperature evaluated by the Penetration Index (PI) (Heukelom nomogram). Figure 15 shows that incorporating lignin into bitumen at different temperatures entails variations in PI. The PI values found are between -1 and +1, meeting the CA-24 Chilean standard (Table 2). It is relevant to highlight that in all the cases analysed and presented in Figure 15, the PI changes from negative to positive for the 20% lignin sample. The lower temperature-susceptible behaviour of bitumen-lignin (20% lignin) explains this behaviour, because the PI is the slope of the temperature-viscosity line in the Heukelom monogram.

Nevertheless, bitumen-lignin samples prepared at 160°C show a higher temperature sensitivity after the RTFO aging than samples prepared at 135°C. In practical terms, the incorporation of lignin makes the bitumen better suited to withstand different climatic conditions. It could lead to improved pavement performance during its lifetime, especially under climate change scenarios with asphalt roads exposed to more extreme temperatures.

Concerning tests associated with the workability of bitumen during asphalt mixture production and, therefore, before aging, Figure 17 shows the results from the rotational viscosity test for bitumen-lignin blends produced at 135°C and 160°C, in the original or unaged state. For samples produces at 135°C the results at both temperatures 135°C and 160°C, demonstrate distinct viscosity levels influenced by the lignin modification. At temperature of 135°C, the lignin modified bitumen recorded a higher viscosity, 0.89 Pa.s compared to the base bitumen, 0.52 Pa.s. Upon increasing the testing temperature to 160°C, both types of bitumen exhibited reduced viscosities; however, the lignin modified bitumen maintained a higher viscosity, 0.28 Pa.s, than its base counterpart, 0.17 Pa.s. This data reflects the inherent differences in flow resistance between the modified and base bitumen across the tested temperatures. For samples produced at 160°C, the results have shown the

same situation as previously discussed. For the base bitumen, the viscosity recorded at 135°C was 0.60 Pa.s, which decreases to 0.20 Pa.s when tested at 160°C. In comparison, the lignin modified bitumen displays a higher viscosity of 0.93 Pa.s at 135°C and 0.27 Pa.s at 160°C. These results indicate that the modified bitumen, even when modified at a higher temperature, retains a higher viscosity at both testing temperatures, suggesting enhanced thermal stability and stiffness due to the modification process. The obtained viscosities indicate that adding lignin to bitumen increases viscosity; however, the viscosity does not exceed 3.0 Pa.s, the maximum viscosity limit established by CA-24 Chilean standards. In other words, bitumen-lignin blends produced at different temperatures maintain workability during the preparation and compaction of asphalt mixtures. Furthermore, the increase in the viscosity may improve the bitumen-lignin performance at high temperatures, enhancing the resistance to permanent or plastic deformation.

3.4.2. Rheological characterization

To evaluate the rheological properties of bitumen-lignin blends, Complex Modulus (|G*|) and phase angle (δ) were measured in the DSR for each sample in both: non aged and RTFO-aged conditions. Figures 18a and 18b show the results for samples prepared at 135°C and 160°C, respectively. As expected, bitumen preparation temperature had an impact on the rheological properties. Analysing this effect found that samples with 0% lignin conditioned to 135°C and 160°C exhibit an increase in |G*|. The phase angle of bitumen-lignin blends prepared at 160°C were similar to those mixed at 135°C, indicating that the bitumen's viscous nature does not significantly change with the preparation temperature of 135°C and 160°C. Conversely, the results of bitumen-lignin samples prepared at 135°C and 160°C and 20% lignin show that lignin's addition increases |G*|,

resulting in a stiffer binder. However, the phase angles remain high (>80°), indicating that 20% lignin content has little effect on bitumen viscous behaviour at the tested temperatures. The phase angles suggest that while the bitumen-lignin may offer improved resistance to deformation resulting from increased stiffness, it still retains dense characteristics that need to be considered in the context of pavement performance at service temperatures.

Overall, DSR rheological results show better performance of bitumen-lignin prepared at the lower temperature (135°C). The test results shown that adding lignin at 135°C effectively enhances the bitumen properties, leading to a superior balance between stiffness and flexibility.

3.4.3. Chemical characterization

Figure 19 presents the FTIR–ATR average spectral ranges per each of the analyzed condition and provides semi-quantitative evidence of the oxidative resistive properties imparted by lignin within the bitumen mixes. Figure 20 presents the results across both processing temperatures of 135°C and 160°C, the modification of bitumen by lignin incorporation results in a semi-quantifiable decrease in the characteristic absorbance peaks associated with sulfoxide (S=O ~1030 cm^{-1}) and carbonyl (C=O ~1700 cm^{-1}) functional groups, which are indicative of oxidative aging pathways in bituminous binders. Each sample was tested six times to assess repeatability and calculate the error, ensuring the reliability of the results.

The sulfoxide absorbance of unaged samples prepared at 135°C with 0% and 20% Kraft lignin was 0.903 to 0.869, while the carbonyl absorbance was 0.975 and 0.952 respectively,

showing an absorbance decrease with Kraft lignin content. Absorbance reduction was also observed on samples with 0% and 20% Kraft lignin and prepared at 160°C. In these samples, the sulfoxide absorbance was 0.907 and 0.853 and carbonyl absorbance was 0.976 to 0.953 for 0% and 20% Kraft lignin, respectively.

The absorbance of RTFOT-aged samples was consistent with the unaged results, showing a reduction in the absorbance of sulfoxide and carbonyl groups when comparing samples with 0% and 20% Kraft lignin. Samples prepared at 135°C showed a reduction in sulfoxide absorbance from 0.892 (0% Kraft lignin) to 0.879 (20% Kraft lignin) and in carbonyl absorbance from 0.979 (0% Kraft lignin) to 0.970 (20% Kraft lignin). For samples processed at 160°C, the average decrease in sulfoxide absorbance was from 0.889 (0% Kraft lignin) to 0.865 (20% Kraft lignin), and in carbonyl absorbance from 0.975 (0% Kraft lignin) to 0.966 (20% Kraft lignin). While the antioxidative efficacy of lignin is confirmed at both 135°C and 160°C, spectral data suggests that these properties are better retained at the 135°C bitumen-lignin preparation temperature. It is proposed that the lower thermal regime may help stabilize the lignin within the bitumen, thereby preserving its antioxidative functionality over extended periods.

The implications of this sustained antioxidative action are significant for the projected lifespan of pavement structure. By forestalling the oxidative degradation, lignin maintains the viscoelastic properties of the bitumen binder, which translates to enhanced resistance to deformation and cracking over the pavement's operational life. The technical preference for a 135°C preparation temperature, in conjunction with lignin modification, is thus underpinned by the dual objectives of immediate oxidative resistance and the preservation of this resistance over time, aligning with the strategic goals of extending pavement life and reducing maintenance frequency. Also, other implication is related to

sustainability because of energy consumption reduction associated to the necessity of execute maintenance and conservation activities during the lifespan of the pavement.

4. CONCLUSIONS

Thermo-chemical behaviour of Kraft lignin was studied considering the different manufacturing temperatures typically associated with the production of several asphalt mixtures, including Half Warm Mixtures Asphalt (HWMA), Warm Mix Asphalt (WMA), and Hot Mix Asphalt (HMA). According to the obtained results, the following conclusions can be drawn:

- Kraft lignin has been widely used as an anti-aging additive because its antioxidant properties are centred on its ability to function as a free radical inhibitor or scavenger during the production process of asphalt mixtures. This attribute is mainly the result of its high phenolic content, which is a fundamental parameter. When this content is reduced by external factors, in this case by exposure to the production temperature of asphalt mixtures, the potential antioxidant capacity of Kraft lignin can be substantially compromised, thereby affecting its efficacy in mitigating free radical-induced damage during the asphalt mixing process and, therefore, its characteristics as an anti-aging additive.
- As explained, Kraft lignin is currently being used in the production of HMA, the mixing temperature of which usually ranges between 150 to 180°C. Considering the findings of this research, the chemical modification of lignin can explain the thermogravimetric effect. Although the effect can be seen in practically all its functional groups, the most relevant impact observed was on the phenolic content.

The experimental results indicate a consequential reduction in phenolic content by more than 20%.

- According to the thermogravimetric differential analysis, within a range of temperatures Kraft lignin remains relatively stable to significant variations in its gravimetric properties without significantly altering its antioxidant efficacy. This temperature range aligns closely with the typical operational temperatures employed in Warm Mix Asphalt (WMA), spanning from 100 to 150°C. Within this spectrum, the lignin stability is most pronounced between 105 and 135°C, indicating that these temperatures are conducive to maintaining its gravimetric properties and, most importantly, its role as an effective free radical scavenger.
- The increased viscosity of the modified bitumen-lignin at the analysed preparation temperatures suggests that lignin increases the bitumen's stiffness, which is expected to enhance the resistance to permanent deformation. Despite the increase in viscosity, the bitumen-lignin viscosity remains within a workable range for producing asphalt mixtures, implying that the bitumen-lignin can be used in asphalt mixtures with appropriate adjustments to the construction practices.
- The rheological results from the DSR tests show that lignin increases the complex modulus (|G*|) of the bitumen, indicating enhanced stiffness which is beneficial for high-temperature pavement performance suggesting improved durability. The phase angle (δ) results reveal that the modified bitumen with lignin retains significant viscous characteristics, which may offer advantages in terms of low-temperature cracking resistance.
- The FTIR-ATR analysis reveals that lignin has antioxidant properties that reduce the formation of sulfoxide and carbonyl groups, which are indicative of oxidative

aging in the bitumen binder. The lower absorbance values for sulfoxide and carbonyl groups in the modified samples suggest that lignin effectively slows the oxidation process, potentially extending the pavement's service life. The values obtained for preparation at 135°C performed better than those prepared at 160°C.

According to these conclusions, an important recommendation emphasizes the development of alternatives within the WMA production temperatures, wherein Kraft lignin exhibited remarkable thermal and chemical stability and effectiveness. In these types of asphalt mixtures, Kraft lignin would maintain its antioxidant properties, especially those related to augmenting its capacity as a free radical scavenger. This situation suggests a potential positive impact on the pavement's longevity, contributing to increased durability and resilience throughout its service life.

Disclosure statement:

No potential conflict of interest was reported by the authors.

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FIGURES

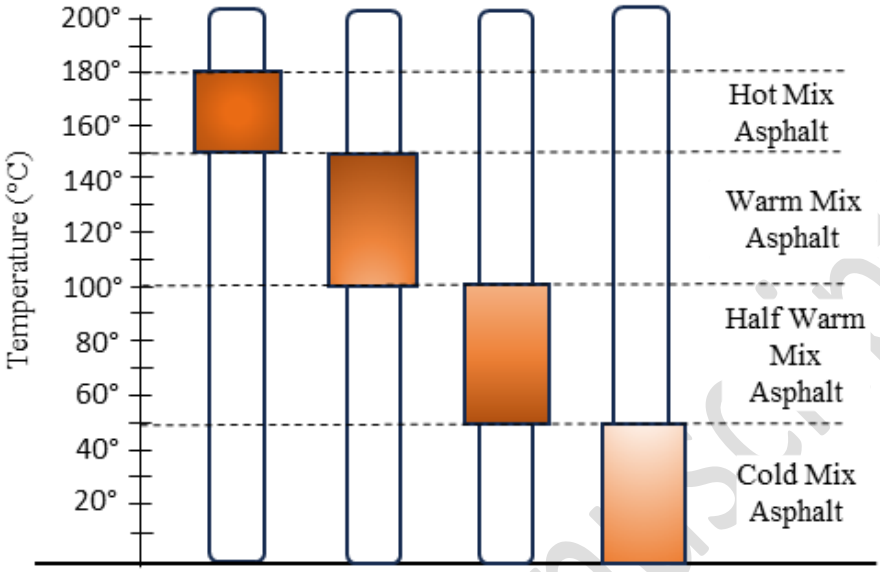


Figure 1: Asphalt mixture classification by production temperature.

Figure 2: Top view of powder Kraft lignin.

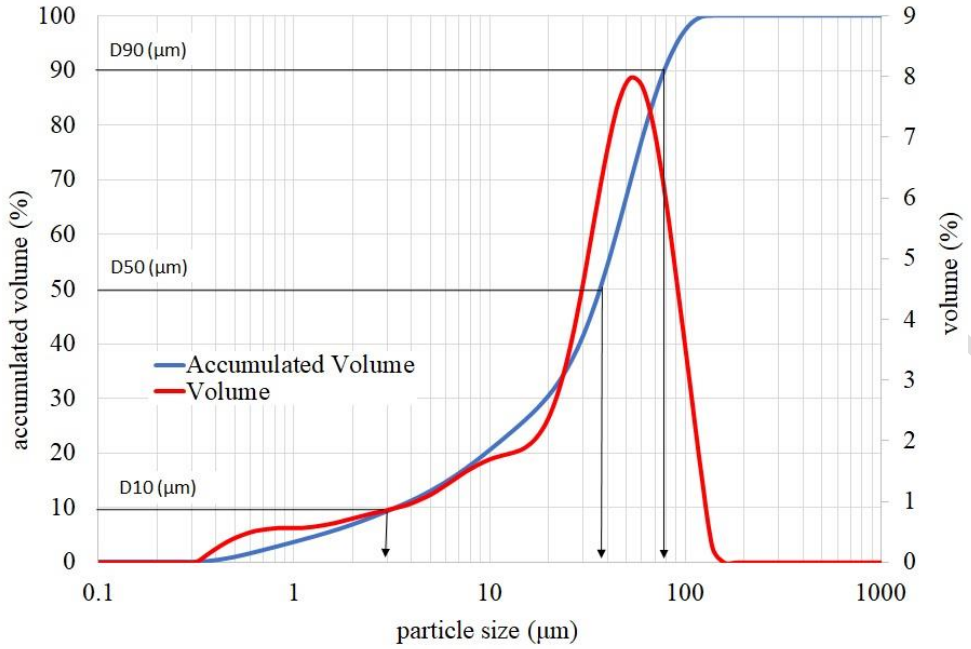


Figure 3: Particle size distribution result for an unconditioned Kraft lignin sample.

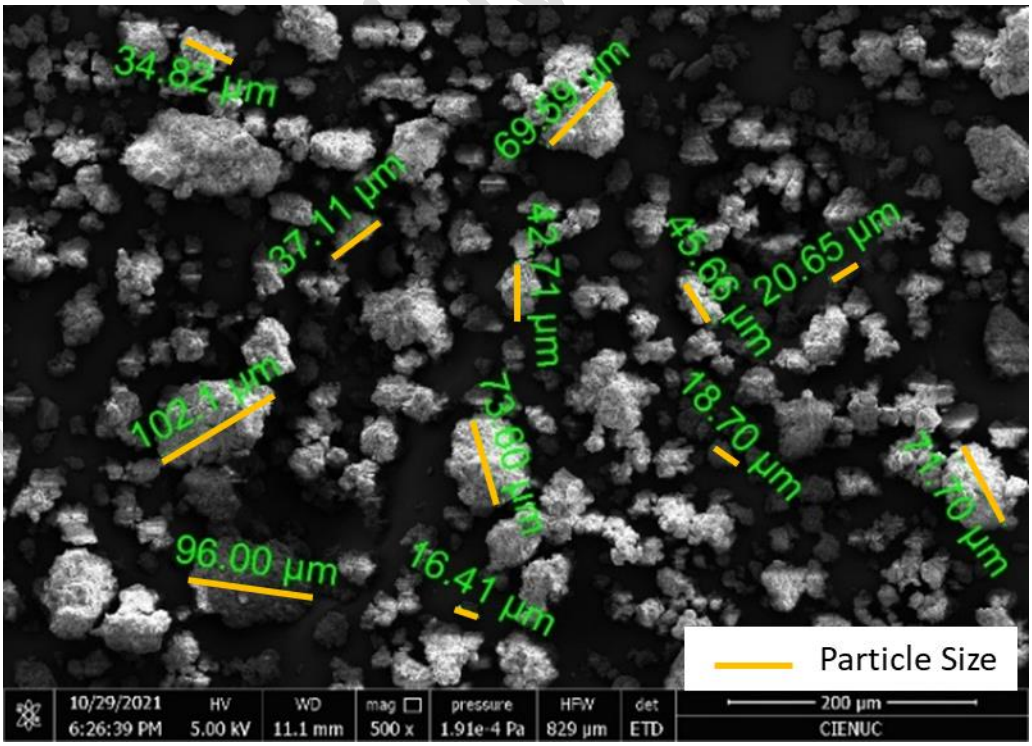


Figure 4: SEM image at x500 for unconditioned Kraft lignin sample.

Figure 5: Kraft lignin samples conditioned at different production temperatures.

(a) (b) (c) (d)

Figure 6: Scheme of the bitumen–lignin sample preparation process: (a) bitumen binder and lignin samples before mixing, (b) mixer, (c) mixing process, and (d) RTFOT conditioning.

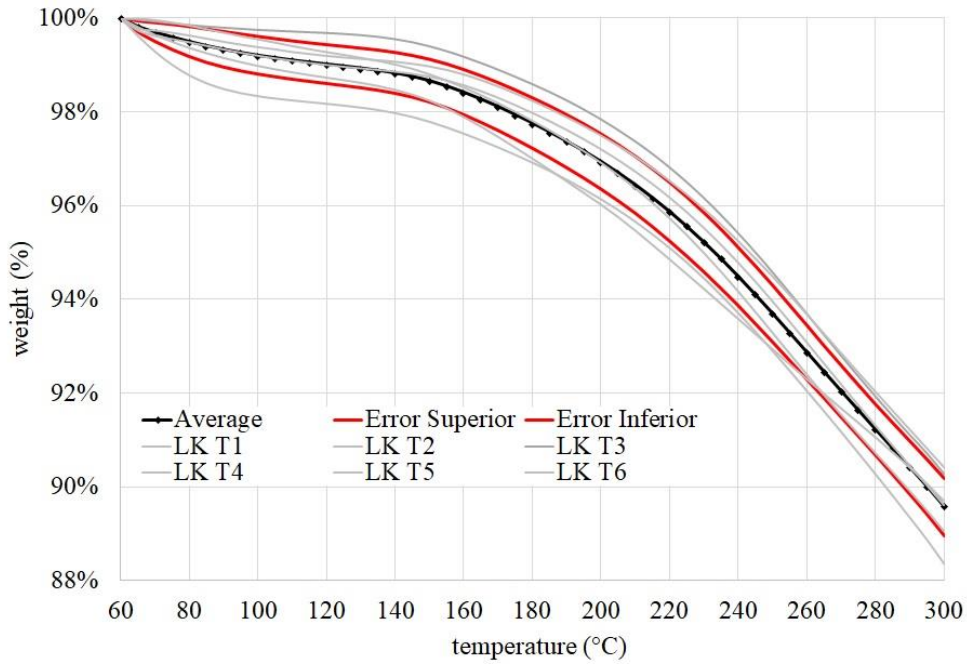


Figure 7: Kraft lignin thermogravimetric analysis.

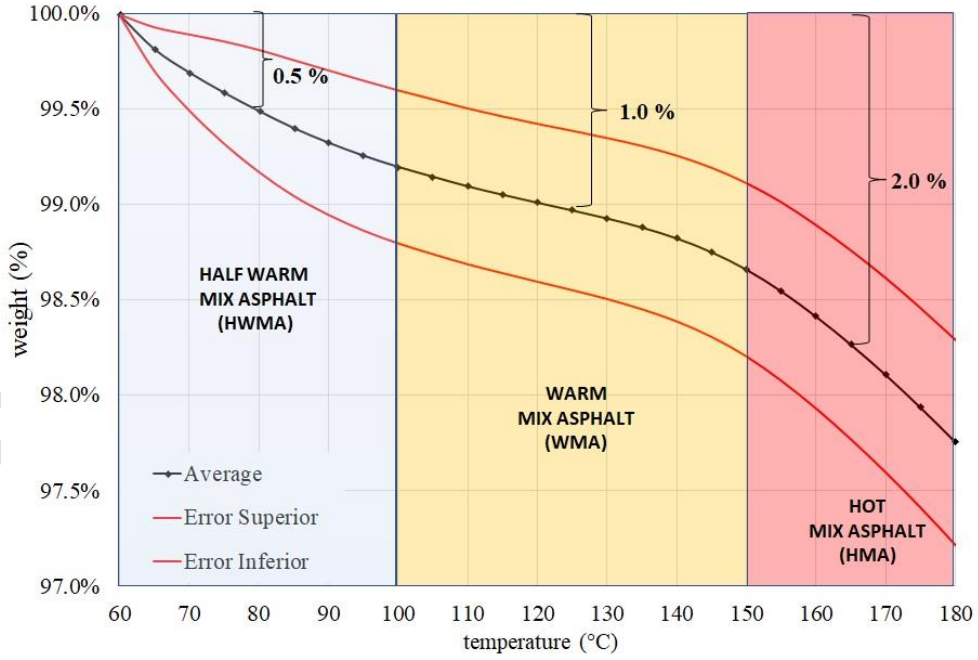


Figure 8: Kraft lignin TGA vs. the production temperature of asphalt mixtures.

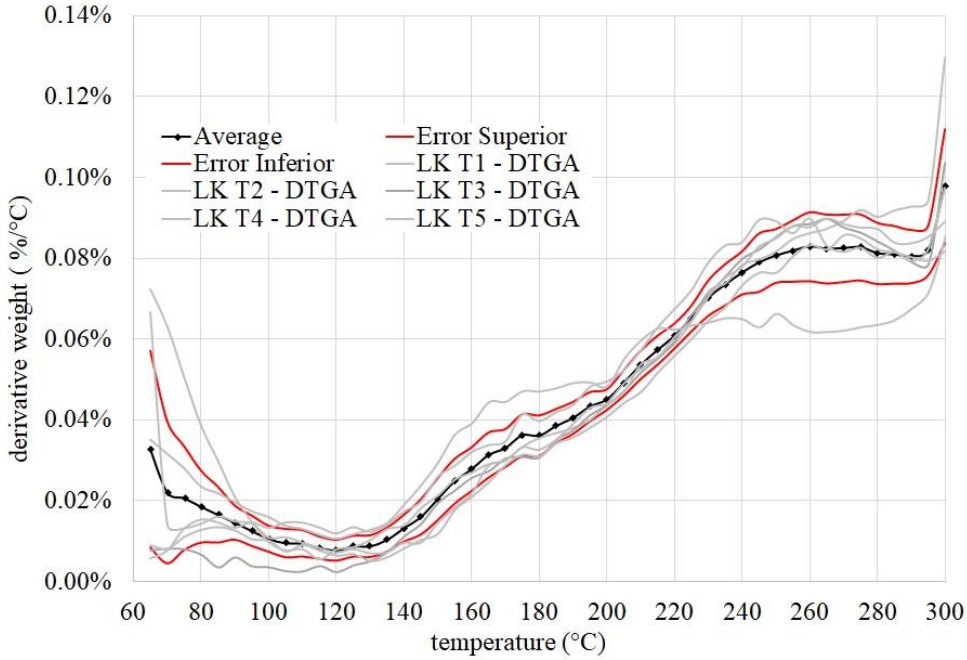


Figure 9: Kraft lignin Differential Thermogravimetric Analysis – DTG.

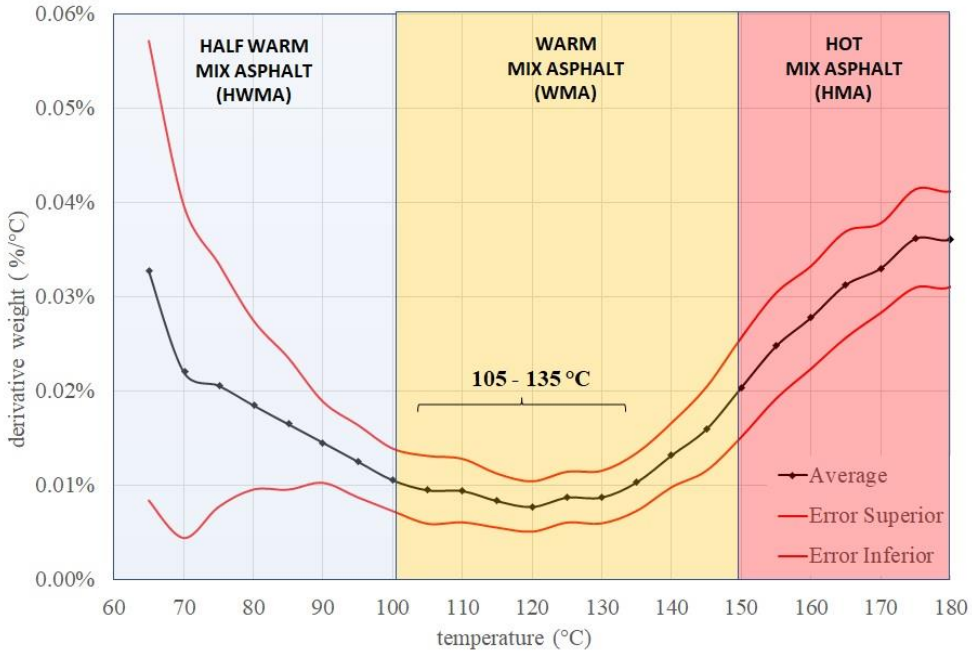


Fig. 10: Kraft lignin DTG vs. production temperature of asphalt mixtures.

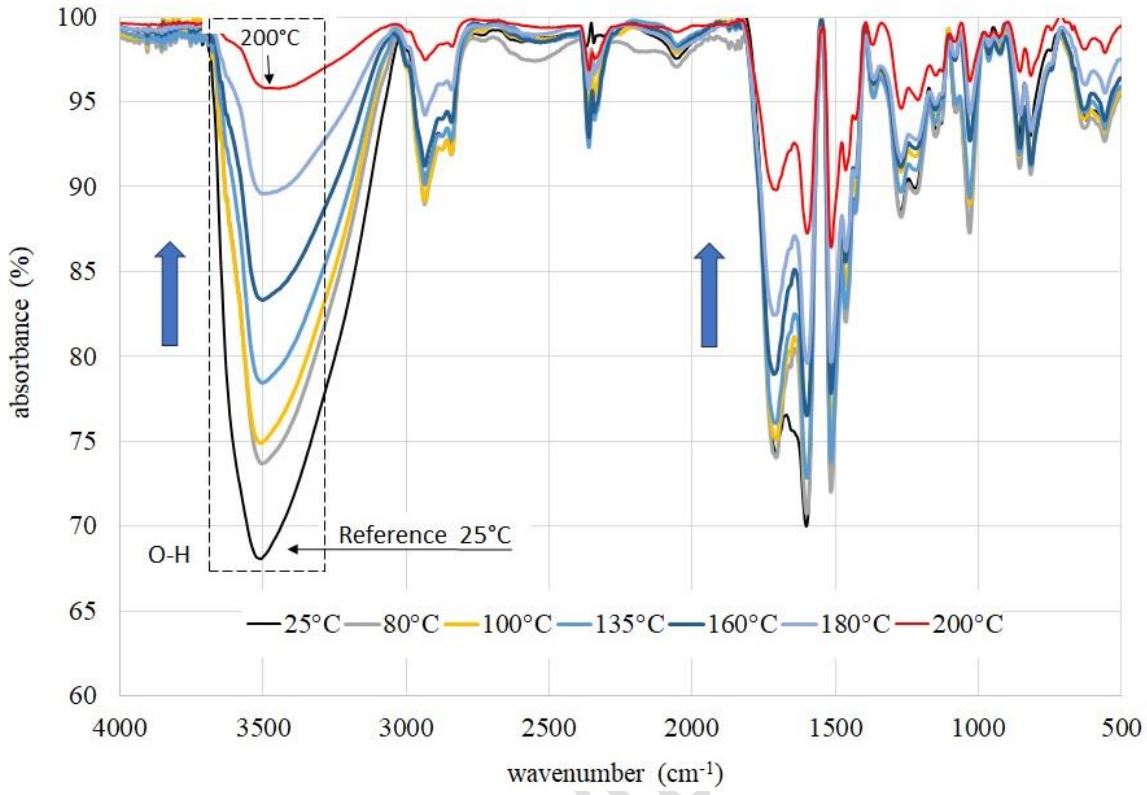


Figure 11: FTIR results of the Kraft lignin exposed to different temperatures.

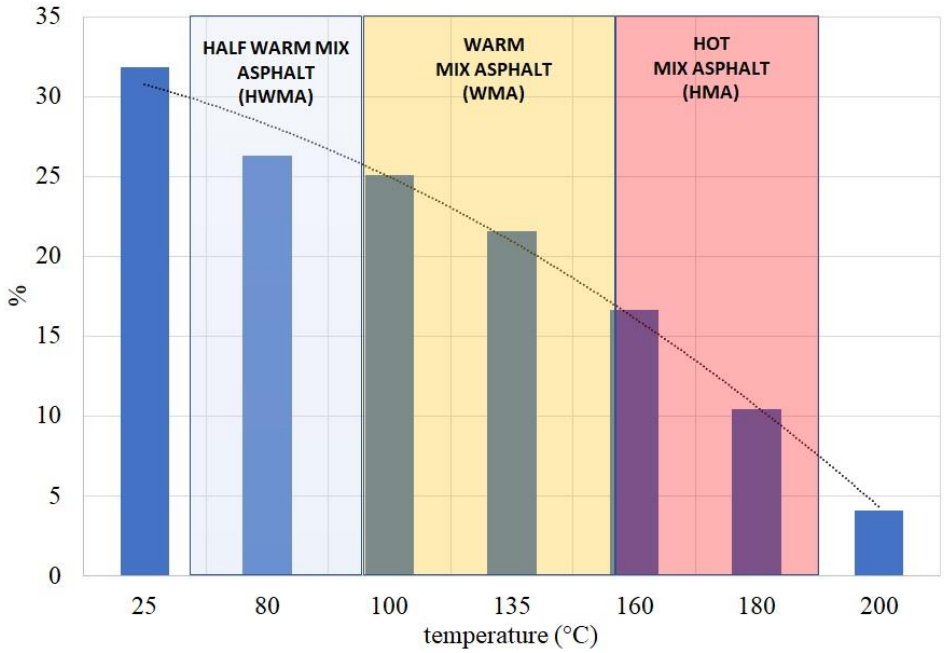


Figure 12: Variation of phenolic content of Kraft lignin from its original condition.

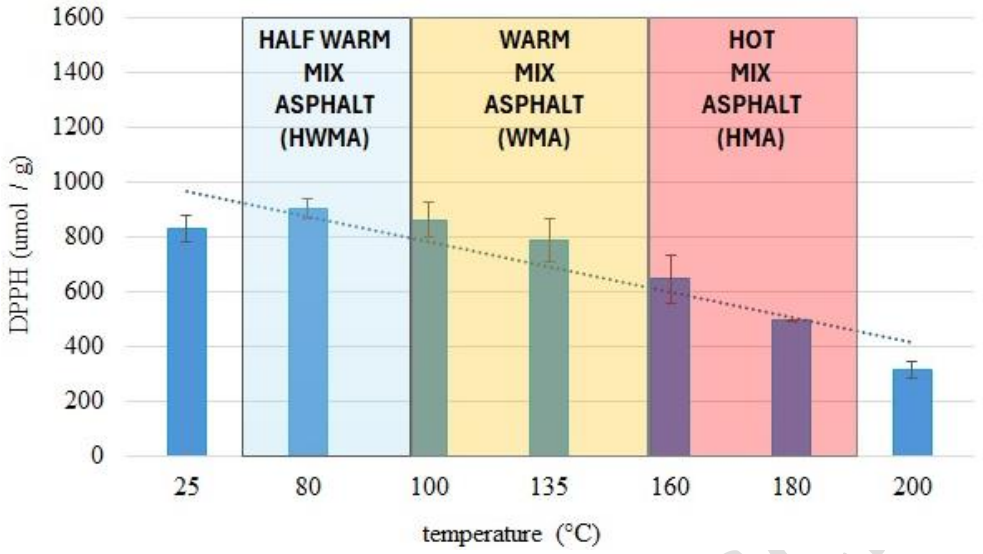


Figure 13: Variation of radical scavenging activity of lignin – DPPH test result.

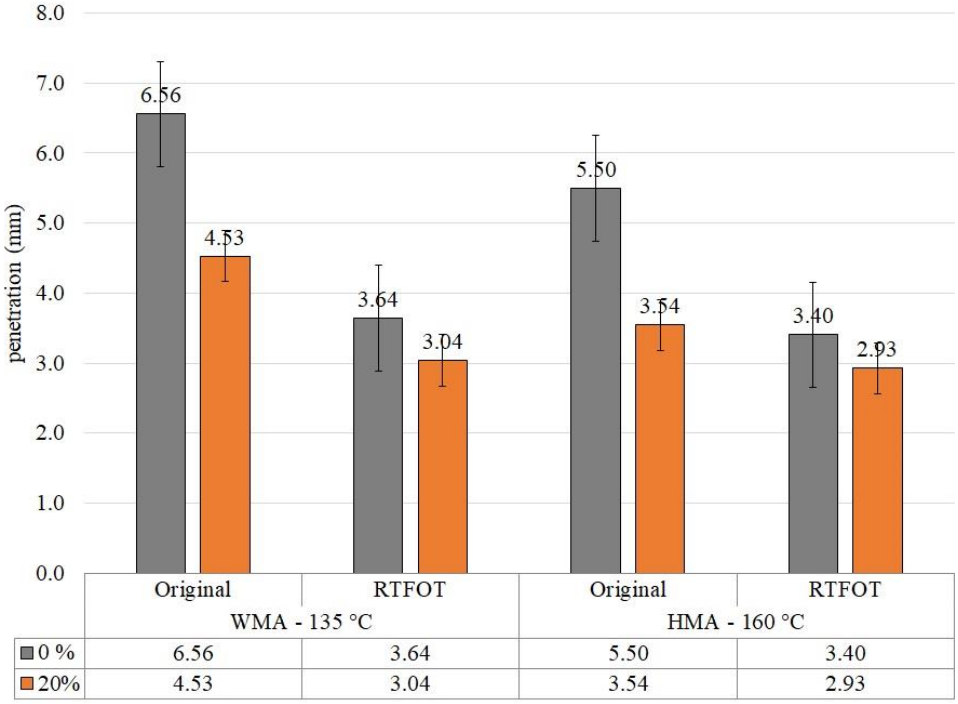
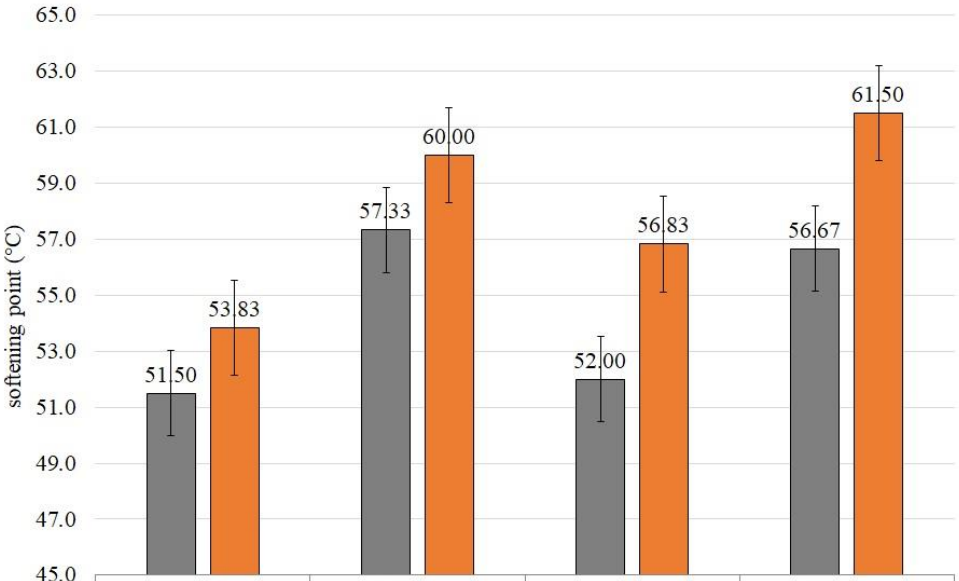
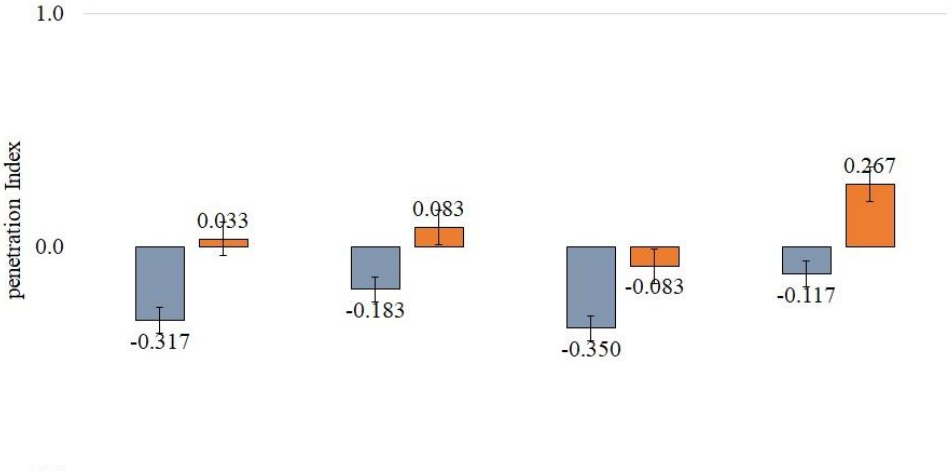


Figure 14: Penetration test results of original bitumen (0% lignin) and Bitumen-Lignin (20% lignin) samples before and after RFTO aging.



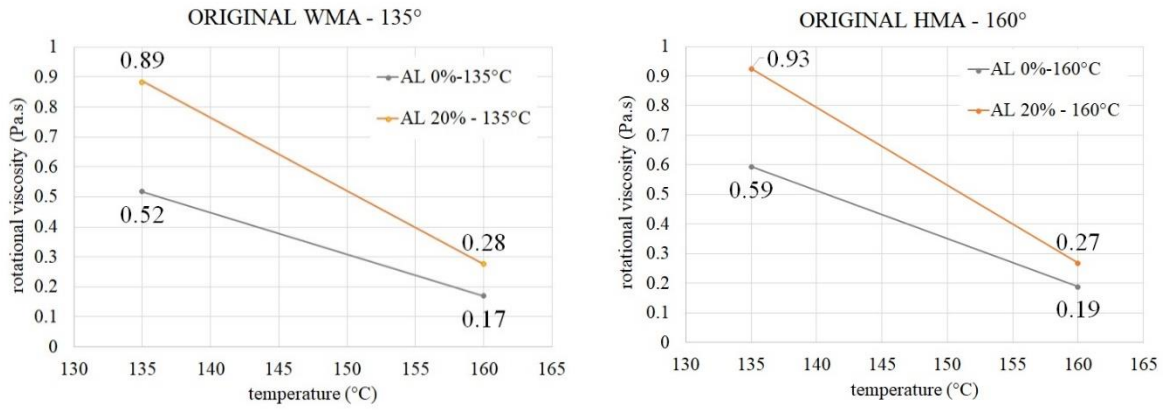
	Original	RTFOT	Original	RTFOT
	WMA - 135°C		HMA - 160°C	
0 %	51.50	57.33	52.00	56.67
20 %	53.83	60.00	56.83	61.50

Figure 15: Softening Point test results of original bitumen (0% lignin) and bitumen - lignin (20% lignin) samples before and after RFTO aging.



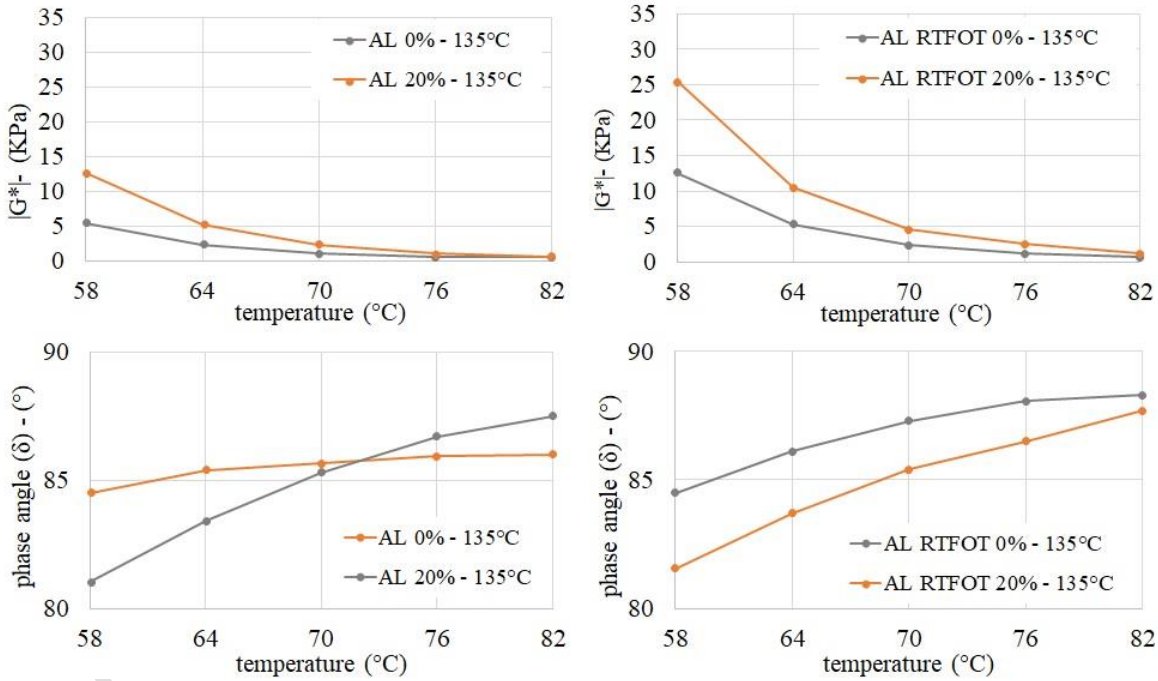
	Original	RTFOT	Original	RTFOT
	WMA - 135°C		HMA - 160°C	
0	-0.317	-0.183	-0.350	-0.117
20	0.033	0.083	-0.083	0.267

Figure 16: Penetration index results for original bitumen (0% lignin) and bitumen-lignin (20% lignin) samples before and after RFTO aging.

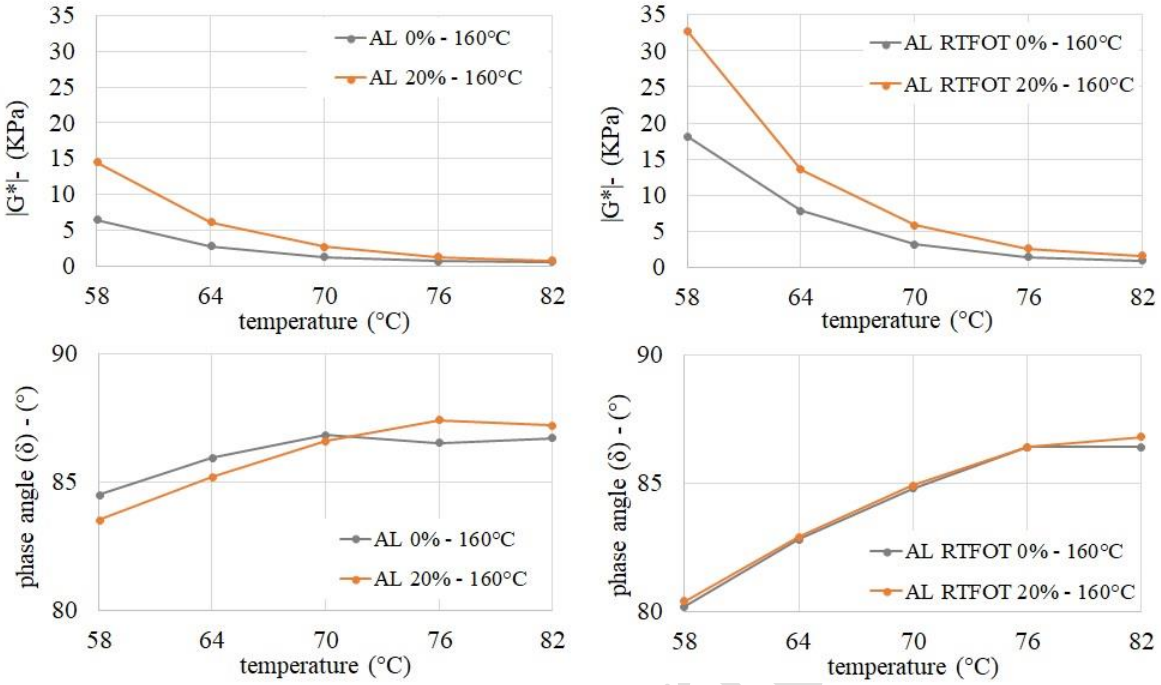


a) b)

Figure 17: Rotational Viscosity for bitumen - lignin blends produced at a) 135°C and b) 160°C, original (unaged) condition.

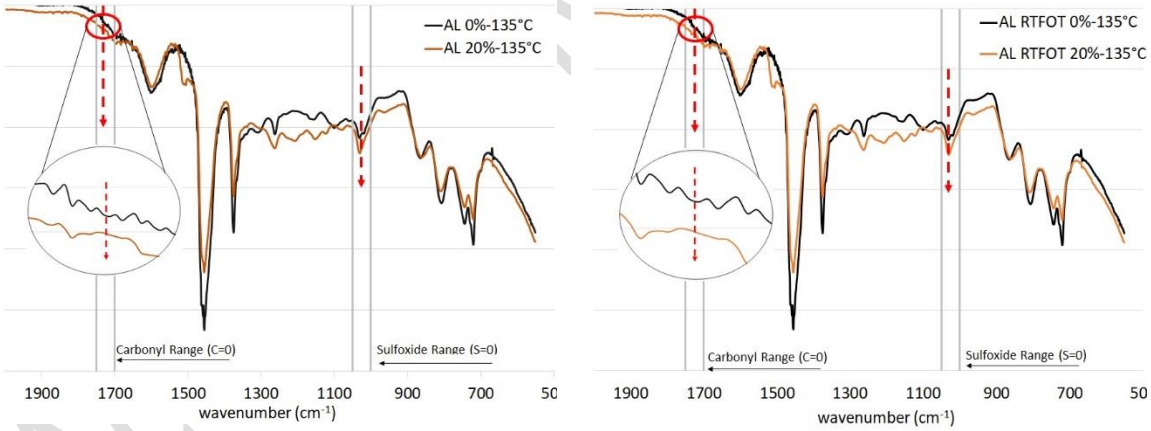


a) 135°C samples

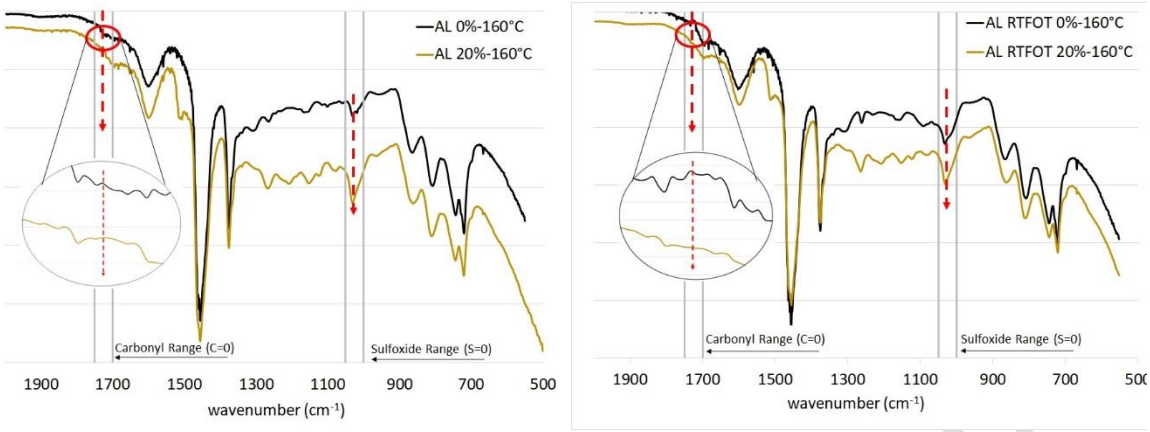


b) 160°C Samples

Figure 18: DSR Results: Complex modulus G* and Phase angle (δ).

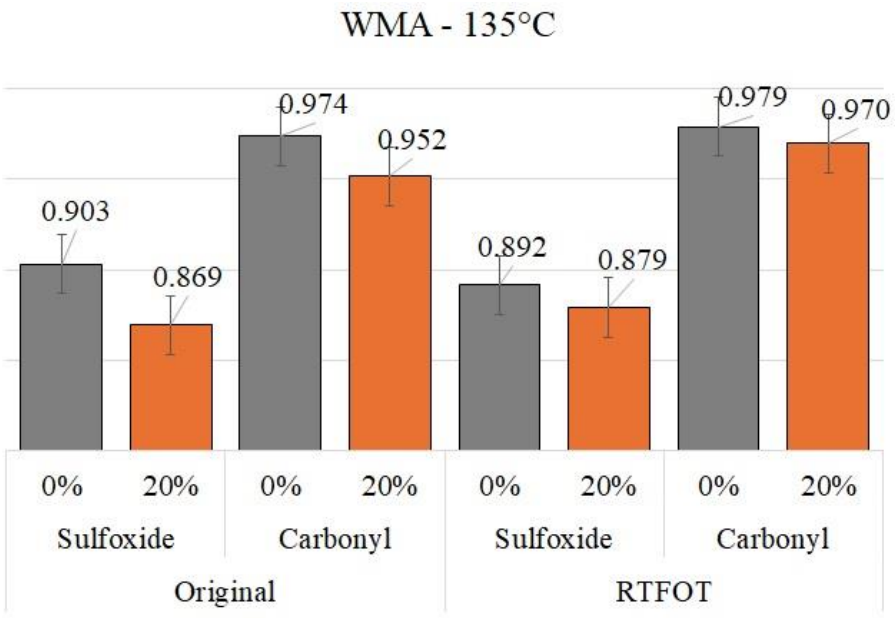


a) **b)**

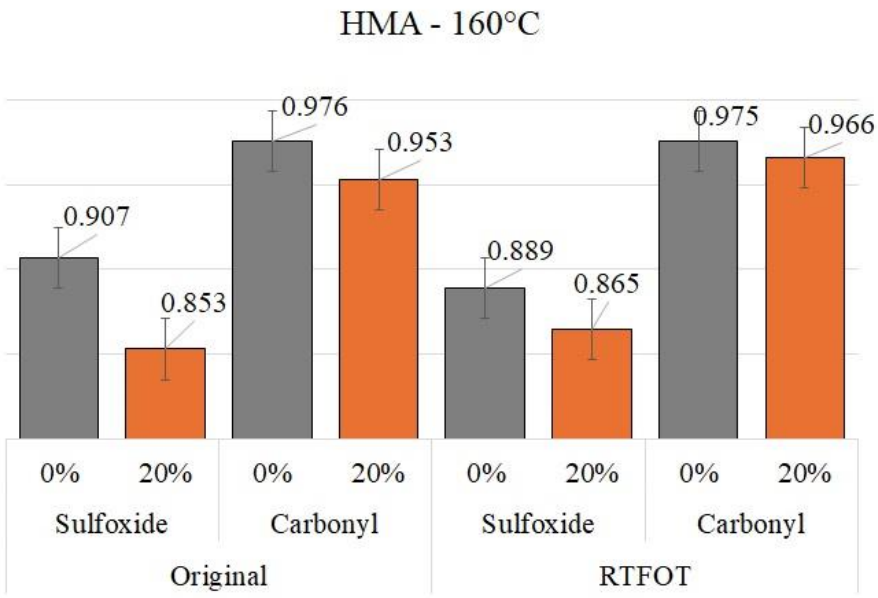


c) **d)**

Figure 19: FTIR-ATR results: a) 135°C samples, b) 135°C RTFOT samples, c) 160°C samples, and d) 160°C RTFOT samples.



a) 135°C Samples



b) 160°C Samples

Figure 20: Sulfoxide and Carbonyl analysis: a) 135°C samples and b) 160°C Samples.

TABLES

Table 1: Kraft lignin elemental components and other characteristics

N°	Description	Value
1	Carbon (%)	63.6 ± 0.1
2	Oxygen (%)	28.3 ± 0.5
3	Hydrogen (%)	5.7 ± 0.2
4	Sulfur (%)	1.4 ± 0.07
5	Nitrogen (%)	0.2 ± 0.006
6	Other elements (%)	0.8 ± 0.00
7	% Water Content (by weight)	25.4 ± 0.1
8	% Ashes Content (by weight)	0.78 ± 0.1
9	Total Phenolic of dry sample (gr catechol/kg)	131± 12
10	pHh Value	3-7

Table 2: Bitumen characterization results

Test	Unit	Result	CA-24 Specification
Unaged			
Absolut Viscosity at 60°C	Poises	3005	Min. 2400
Penetration at 25°C, 100g, 5s	0.1 mm	51	Min. 40
Softening Point	°C	50.4	-
Flash point	°C	> 232	Min. 232
Ductility at 25°C, 5 cm/min	Cm	150	Min. 100
Penetration Index	-	-1.1	-2.0 to + 1.0
RTFOT			
Mass Loss	%	-0.46	Max. 0.8
Absolut Viscosity at 60°C	Poises	10377	-
Ductility at 25°C, 5cm/min	Cm	> 100	Min. 100
Durability Index	-	3.5	Max. 4.0

Table 3: Bitumen characterization tests performed on bitumen modified with Kraft lignin.

Test	CA-24 Specification	Description
Penetration	MC – 8.302.3	The penetration test is used as a measure of the consistency of bitumen behaviour. High penetration values indicate softer consistencies.
Softening Point	MC – 8.302.16	The softening point test determines the temperature at which asphalt binder softens to a specified degree under the weight of a steel ball. This test is effective for assessing bitumen's heat susceptibility and performance at elevated temperatures
Penetration Index	MC – 8.302.21	The Penetration Index (PI) quantifies the temperature susceptibility of bitumen. A low PI indicates high temperature susceptibility, which can lead to brittleness and cracking in colder climates
Rotational Viscosity at 135°C	MC – 8.302.24	Rotational viscosity measures the resistance of bitumen to rotational shear at high temperatures. This test ensures that the bitumen is fluid enough for proper mixing and compaction during asphalt mixture production
Rotational Viscosity at 160°C	MC – 8.302.24	
Rheological properties using a Dynamic Shear Rheometer (DSR)	MC – 8.302.22	The Dynamic Shear Rheometer (DSR) test measures the viscous and elastic behaviour of bitumen at different temperatures. This test is critical for evaluating bitumen's performance.

Table 4: Kraft Lignin Thermogravimetric Analysis.

N°	Description	Production Temperature (°C)	% Loss of Weight	Δ% Loss of Weight
1	Half Warm Mix Asphalt (HWMA)	60 – 100	100.0 - 99.2	0.5 ±0.3%
2	Warm Mix Asphalt (WMA)	100 – 150	99.2 – 98.7	1.0 ±0.4%
3	Hot Mix Asphalt (HMA)	150 – 180	98.7 – 97.8	2.0 ±0.5%