

CHALMERS UNIVERSITY OF TECHNOLOGY

MASTER'S THESIS PROJECT FOR MATERIALS CHEMISTRY MPMCN

A LABORATORY AGING PROCESS OF LIGNIN-INTEGRATED ASPHALT

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Abstract

Climate goals in industry are a powerful driving force in the development of new industrial processes. The Swedish Transport Sector has setup the goal of becoming CO₂ neutral by the year 2045. Thus, the asphalt industry must develop more sustainable materials and processes. Lignin has the potential to act as an extender to the asphalt binder as well as an antioxidant with radical quenching potential. This thesis will therefore investigate the impact lignin has on the asphalt throughout its service life. A method for simulating the accelerated ageing behaviour of asphalt pavements with the binder bitumen, partially replaced with lignin, was therefore designed and evaluated. The thesis includes a literature study and an experimental trial. First, the literature study was conducted in order to find the factors and mechanisms, leading to ageing in asphalt pavements as well as methods for ageing asphalt samples in a laboratory setting. The review found the ageing behaviour for in-field asphalt is the so called "long-term ageing" in which, oxidation is the main ageing mechanisms. Thus, most ageing methods use elevated pressure or temperature to accelerate the oxidative behaviour.

In the experimental part; the long-term oven test was selected as the ageing method. Thus, three batches of asphalt were produced: in two of the batches lignin was integrated into aggregate mix to reduce the bitumen content. Hence, the batches contained 10 wt% and 25 wt% lignin by binder weight respectively. The third batch was a conventional asphalt pavement used as a reference. All three batches were analysed when both aged as well as when non-aged using Cantabro Mass Loss, Prall and the Indirect Tensile Strength Ratio tests to assess the impact ageing has on the mechanical properties of asphalt. Furthermore, bitumen from all batches were separated from the aggregate mixture in order to evaluate the binders with softening point test and infrared spectroscopy. Results from the IR spectroscopy verify the efficacy of the ageing method. Oxidation has occurred on all aged samples. Furthermore, the softening point test verified the hypothesis from the literature review in that ageing lead to increased polarity in binders from all asphalt samples. The mechanical testing were less conclusive as they also relate to the air void contents in the asphalt pavement. All asphalts showed a deterioration in the Cantabro test after ageing. Hence, the asphalts are less ductile. In the Prall test both lignin batches improved their abrasive resistance after ageing whilst, the opposite was observed in the reference batch. Lastly, the indirect tensile ratios decreased from ageing in all samples.

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1 Introduction

Durable and functional roads are necessary for the development of infrastructure in any country. By improving the conditions for transport; commerce, trade and movement of both people and goods becomes easier and more efficient. Today about 90% of the worlds highway construction consists of asphalt pavements¹. Furthermore, the global production for asphalt was set to grow into 100 million tonnes in the 2010s. With markets in China, India, Brazil and Eastern Europe growing steadily, asphalt will be needed to sustain the construction of roadway infrastructure in the nearest future². In western countries such as Sweden, paving companies are in a transitional period, where they are reducing their environmental impacts to be CO₂ neutral by the year 2045³. Furthermore, up to 20 % of these emissions comes from the fossil-based binder bitumen. In order to reach the climate goal, the production of asphalt needs to reduce its energy demand in paving as well as in production and substitute the constituents in asphalt for more sustainable alternatives or to simply extend the service life of the asphalt pavement. A paper by Rushing et al found about 80 % of deterioration in airstrips came from non-load related stresses, whereas load-related stress only accounted for 5 to 15 %. Thus, the physical and chemical properties of the components in asphalt pavements will be important for its longevity⁴. In this thesis the content of asphalt binder (bitumen) is reduced by integrating lignin into the asphalt matrix. In order to verify its efficacy in the field, the lignin-integrated asphalt must undergo an ageing process capable of simulating 10 years worth of service. Since no standardized ageing process exists in the asphalt industry, the main focus of this paper is to develop such an ageing process and verify its efficacy using Fourier transfer infra-red spectroscopy (FTIR), softening point measurements and mechanical testing.

1.1 Asphalt Chemistry

Foundations of bitumen (natural asphalt) were found in Trinidad and were used for road paving by the eighteenth century. By the early 20th century asphalt pavements and asphalt concretes had become the most common material for the paving of roads. Today's asphalt concrete consists of multiple components with the most basic components being the asphalt binder and aggregate particles. The aggregate particles makes up close to 95 wt% of the asphalt pavement. Thus, having a big influence on the asphalts properties.⁵ These particles should be thoroughly crushed rock particles of cubical form, as opposed to long and flat. Thus, allowing for better interlocking between aggregate particles and hence increasing strength and rut resistance. As the aggregates carry most of the loads in pavements, unnecessary defects and impurities must be avoided. Hence, the crushed stone or gravel must be thoroughly cleaned to remove any clay, dust and dirt from the aggregates before mixing with the asphalt binder⁵. It's also important to take the aggregate particles properties into account when choosing components for the asphalt mix. Since, the mechanical properties of aggregates have been found to carry over to the asphalt concrete, particles with high toughness and abrasion resistance should be considered. Mixes with high toughness are less likely to break down during the construction process, hence leading to an asphalt with better resistance to pop-outs (small shallow pits in the pavement surface) and raveling, thus reducing the risk of moisture damage as well as being less likely to polish under traffic. This is hugely important to maintain good skid resistance and minimizing the damaging effects from freeze and thaw cycles⁵. Additionally, mineral fillers are added into the asphalt mixture. These usually come in the form of rock dust, slag dust, hydraulic cement, hydrated lime and fly ash. By adding this very fine inert material, the density and strength of the asphalt binder can be improved as it forms a mortar or mastic and thus, stiffens the material.

The overall structure design of asphalt pavements are not that of a completely uniform material. In fact multiple layers often referred to as courses make up the material. Three courses are present in all asphalt concretes *i*) surface course, *ii*) base course, *iii*) sub-base course. Occasionally a

fourth grade, the so called binder course may be added. The surface layer is the top layer as well as the wearing layer. Thus, it requires the highest-quality materials and the highest binder content. It's main requirements are *i*) wet weather friction, *ii*) resistance to load-induced rutting, shoving and surface cracking, *iii*) resistance to thermally induced cracking, *iv*) resistance to disintegration due to ageing, traffic loads and freeze-thaw effects, *v*) surface texture for noise control and safety, lastly *vi*) smoothness. All of these factors in some way or an other relate to friction and mechanical resilience. Thus, the aggregates used are highly angular to provide good interlocking, furthermore the aggregates must be polishing resistant in order to maintain good skid resistance and good friction. Effects from weather such as air, sunlight, temperature changes and impermeability towards water. The base course is the second layer from the top and provides sub-surface drainage of water and distribution of load bearing from traffic. Since the base course is the main load bearing layer in asphalt pavements it must be durable and resistant to bottom-up fatigue cracking. Rut resistance is however not necessary as the layer is not in direct contact with traffic. Occasionally a binder layer is placed between the surface course and base course. It helps delaying reflective cracking and improves pavement smoothness. Furthermore, the binder layer uses much lesser amounts of asphalt binder since the layer has no requirement on resistance to rutting and the effects of water and oxidation. Lastly, the sub-base course is the lowest layer in the pavement and supports the base-layer with load bearing. Furthermore, the sub-base layer prevents the intrusion of fine materials e.g. sand into the upper layers⁵. This thesis will only investigate the surface course, as the ageing of asphalt occurs on the asphalt surface.

1.1.1 Asphalt Binder

Asphalt binder goes by different names in different regions. In North America it is simply called asphalt, in Europe however, it is referred to as bitumen. In this thesis the terms bitumen and asphalt binder will be used. As the name implies; asphalt binder holds the material together. By increasing the temperature of the bitumen the viscosity is very low similar to that of paint or lubricating oils and can thus, easily coat the aggregates, allowing the binder to absorb into the aggregate. When the temperature is then reduced to ambient levels, the bitumen stiffens and its viscosity increases significantly and the bitumen which now behaves like a non-mobile liquid e.g. peanut butter sticks to the aggregates and holds them in place. Thus, binding the asphalt pavement together⁵. Furthermore, the binder is characterized by a penetration grade. This test applies a load to the bitumen sample at a specific temperature for a specific time, where the penetration is measured at closest 0.1 *mm*. Thus, the penetrated depth into the bitumen becomes the grade. For example a bitumen with grade 100/150, has a lowest penetration of 10 *mm* and a deepest penetration of 15 *mm*. The penetration grade is indicative of the hardness of the bitumen sample and is used to determine its suitability for various climates.

Bitumen is typically sourced from residues in the petroleum refinery processes. The composition of bitumens vary depending on the source of crude oils they were refined from. Notably there are four general classifications of compounds in the components of bitumen. Note that these are not chemical classes of compounds but general classes⁵. As such compounds are not assigned a class based on their structure. Instead they are assigned to a class based on their polarity. Aromatics for example are aromatic compounds. However aromatic compounds may still be found in the other fractions⁶. The four fractions in bitumen, typically called the SARA fractions are in order of rising polarity:

- Saturates: Contains linear, branched and cyclic saturated hydrocarbons (paraffin).
- Aromatic and naphthalene compounds: Consists of partially hydrogenated aromatic compounds.
- Resins: Polar aromatic constituents which, contain various functional groups.

- Asphaltenes: Contains high molecular weight polar functional groups and hetero-cyclic compounds.

In a study by Fu et al. the average molecular structures of the SARA fractions were investigated using, FTIR, H-NMR, GPC and elemental analysis⁷. These proposed average structure should however, be taken with a grain of salt, since they are not the real structures. But as approximations they may provide some insight and a basis into some structure-related properties.

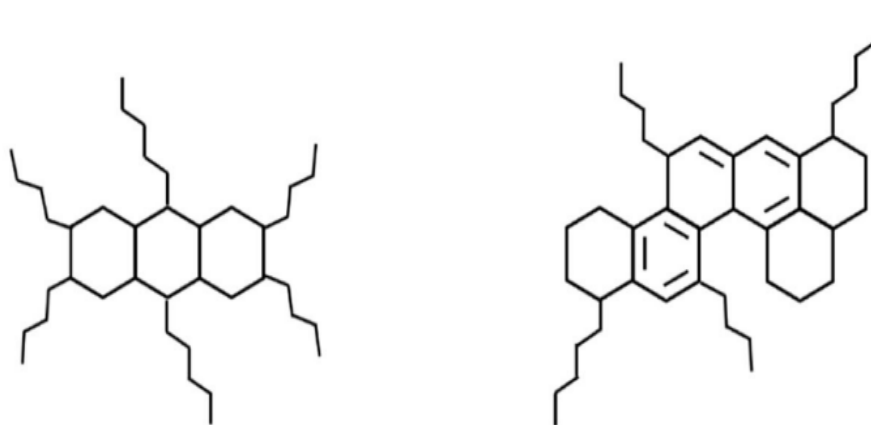


Figure 1: Average molecular structures of Saturates (Left) and Aromatics (Right) as proposed by Fu et al.⁷

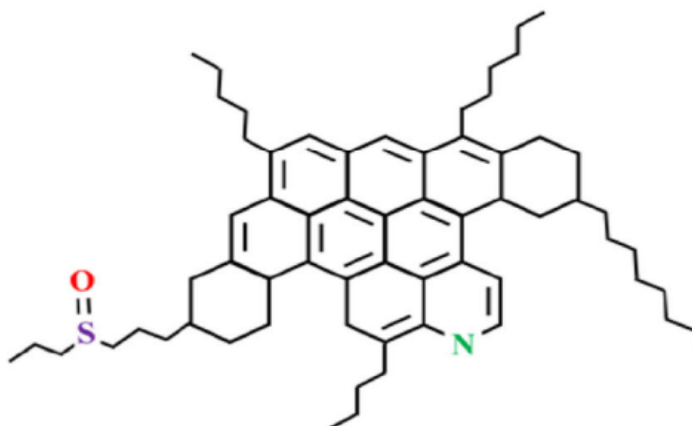


Figure 2: Average molecular structures of Resins as proposed by Fu et al.⁷

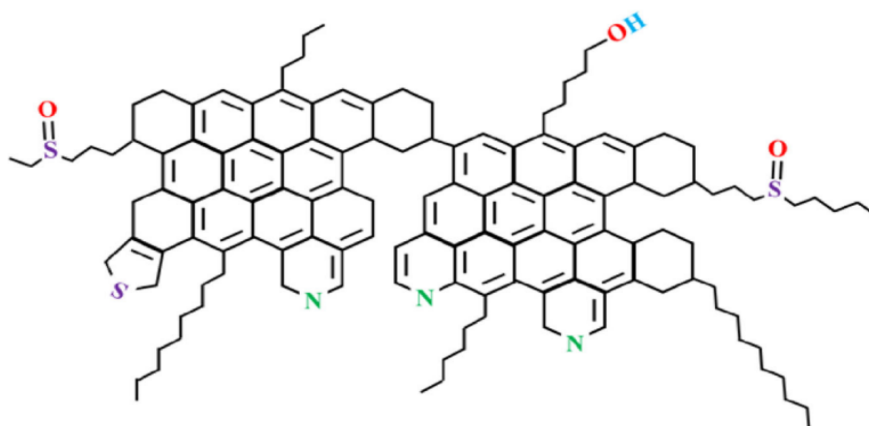


Figure 3: Average molecular structures of Asphaltenes as proposed by Fu et al.⁷

Various studies have been conducted with the goal of describing the effect of the respective SARA fractions, whose structures are described by Figures 1, 2 and 3 respectively. A literary review by Xiao et al. summarized various findings.

Apolar fractions: Saturates and Aromatics, contribute to plasticising effects, lead to viscous behaviour. Furthermore, higher Saturate content lead to a decrease in viscosity and lower glass transition temperature⁶.

Polar fractions: Resins and Asphaltene, lead to increased stiffness and tensile strength, asphaltenes lead to higher viscosity as well as elastic behaviour. Furthermore lower asphaltene contents were linked to brittleness as well as lower glass transition temperature which, increase with increasing asphaltene content⁶.

1.2 Lignin

The naturally occurring polymer lignin can be found in the cell walls of trees, where it makes up between 25-33 wt% of the tree⁸. Lignin has become a very attractive feedstock for the production of chemicals and polymers. Mainly, due to its complex structure thus, providing a direct source for phenols and aromatic compounds. Furthermore, lignin contains building block which can be used in various substitution, oxidation and addition reactions. Even the material itself has gathered attention for its inherent properties e.g. rheological, adsorption and adhesive properties. Thus, lignin shows great potential for composite materials such as dispersants, emulsifiers, additives, adhesives and binders⁹. Lignin is commonly produced using the Kraft pulping process wherein lignin is separated from cellulosic fibers, in order to produce a pulp suitable for paper production. First white liquor, an aqueous mixture of NaOH and Na₂S, is reacted with wood chips under high pressure and temperatures. The lignin is split into smaller water/alkali-soluble fragments. Thus, free phenolic hydroxyl groups are generated leading to an increase in hydrophilicity of the lignin and lignin fragments. Lastly the lignin and lignin fragments are separated by three cooking phases at elevated temperatures, until 95 % of the lignin is removed¹⁰. Despite multiple industries such as carbon fibers, adhesives and plastics are researching the implementation of lignin, no commercially viable products have been developed¹¹. As such most lignin is burned in heat and power plants to generate heating and electricity⁸.

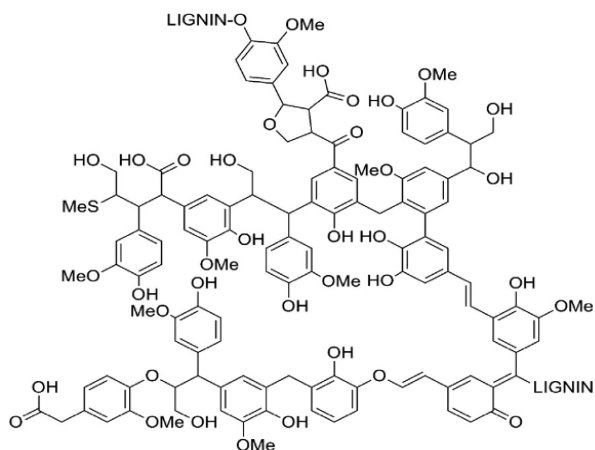


Figure 4: Molecular structure of Kraft Lignin as proposed by Crestini et al.¹²

Lignin can from a structural standpoint show great promise as an antioxidant. Kraft lignin contains numerous phenolic compounds. Thus, lignin should be able to scavenge oxygen containing free radicals by donating either a proton or an electron, whilst remaining relatively stable¹³. That being said, lignin has been shown to decompose at elevated temperatures. Temperatures over 150 °C usually lead to heavy oxidation of the lignin sample. Since asphalt production can have temperatures of 160 °C, mixing must occur at lower temperatures. Furthermore, lignin has been utilized as an additive for the polymer, plastics and rubber industries. Since, polymeric rubbers have a high content of reactive C=C bonds, they are prone to degradation through radical reactions, usually followed by cross-linking. Lignin additives have been found to scavenge oxygen-induced radicals, and thus prevents formation of cross-linking. Reduced density in cross-links have been linked to improved flex crack resistance due to increased stress relaxation as the amount of cross-linking decreased¹⁴. This study will utilize the lignin as a filler material, with the hopes of finding a functional role for the lignin as an anti-ageing radical quencher and as an extender to the bitumen.

1.3 Ageing Factors

The rheological behaviours of most viscoelastic materials are influenced primarily by temperature and time, exhibiting soft behaviours at high temperatures and stiff behaviour at low temperatures. This is the case with asphalt where its high thermal absorptivity results in plastic deformation under vehicle loading influence. Such stresses usually comes in the form of rutting and cracking. This plastic deformation in combination with the sensitivity of its hydrocarbons to factors such as e.g. heat, oxygen, solar radiation and water leads to asphalt becoming more stiff and brittle over time. Thus, leading to fatigue- and low-temperature cracking. This change in rheological behaviour over time is referred to as ageing¹⁵.

Some of the more common factors that results in the ageing of asphalt is; oxidation, volatilization, thixotropy, polymerization and separation¹⁶. With the three main factors being oxidation, volatilization and thixotropy.

- Oxidation: The asphalt component reacts with oxygen from the air and becomes irreversibly altered in the physical and mechanical properties. This oxidative ageing is believed to be caused by the incorporation of oxygen by the sulphurs and hydrocarbons in the asphalt, thus increasing the polar-functionality on asphalt component molecules leading to increased chemo-physical associations such as hydrogen bonding and Coulombic interactions. Thus, resulting in agglomeration of molecules at the surface layer, causing cracks¹⁶.

- Volatization: Lighter components in asphalt evaporates and escapes into the atmosphere when the asphalt is heated to high temperatures. The weight loss results in an increase in viscosity and modulus. This phenomenon is mostly observed during mixing of asphalt binder and aggregates. Thus, volatization is related to short-term ageing¹⁶.
- Thixotropy: Thixotropy also referred to as steric hardening is the phenomenon where asphalt reorganizes its structure. This is mostly observed at lower temperatures and leads to increased viscosity and hardening of the asphalt. Thixotropy can be reversed through heating and agitation¹⁶.
- Moisture Damage: Water diffuses into the asphalt resulting in a loss of cohesion in the asphalt mixture or loss of adhesion between the asphalt binder and the aggregate¹⁷.
- Polymerization: Smaller molecules combine into larger macro-molecules with repeating units. The polymerization occurs in asphalt due to actinic light and due to heat¹⁶.

A paper by Menapace and Masad evaluated the ageing properties of asphalt binder through the use of atomic force microscopy. They found a thick film forming at the surface of the binder. As expected the film had a chemical composition different from the un-aged binder displaying larger molecules containing larger amounts of oxygen, due to oxidation and polymerization. What's more, the paper found an interaction between ageing factors contribution increasing when more factors were introduced. For example UV-radiation and elevated temperatures lead to more oxidation than compared to only ageing the asphalt binder under UV. An ageing protocol of 2 days of UV radiation at a temperature of 40-50 °C would lead to comparable ageing to a protocol of only UV at ambient temperature for 15 to 30 days¹⁸. Mastrofina and Scarsella found a correlation between SARA fractions and ageing. In their paper they found saturates and aromatics are transformed into resins. Furthermore, resins are in turn converted into asphaltenes¹⁹. Thus, the polar fractions of bitumen would increase with degree of ageing.

1.4 Laboratory Processes for Ageing Asphalts

There are multiple methods that lead to ageing of asphalt. Naturally, it's not possible to mention all methods. Hence, the most common and most promising ageing methods will be briefly mentioned in the section below.

1.4.1 Short-Term Ageing Processes

Short-Term ageing is the deterioration in rheological properties which, occurs when asphalt binder is mixed with hot aggregates during asphalt production. This occurs because a very thin-film of asphalt is in contact with air whilst at an elevated temperature¹⁶. Thus, oxidation and volatization are the main mechanisms for short-term ageing of asphalt mixtures. Laboratory methods for testing short-term ageing of asphalt binders are described below:

1.4.1.1 Thin Film Oven Test The standardized Thin Film Oven Test (TFOT) examines a 50 mL sample of bitumen in a flat container resulting in a film thickness of roughly 3mm. The sample is then subjected to an elevated temperature of 163 °C for 5 hours whilst rotating at a speed of 5 rpm. The main strength as well as the main drawback of the TFOT method is volatization. Elevated temperature for prolonged amounts of time results in lighter molecules escaping the asphalt mix. Since, volatization is the main mechanism for ageing during asphalt mixing and paving, the TFOT is an excellent tool for simulating short-term ageing behaviours. In the long-term ageing it is lacking in some regards. Temperatures are usually low during the service life of asphalt. Hence, very little volatization occurs¹⁷.

1.4.1.2 Rolling Thin Film Oven Test This modification of the TFOT test places the sample in a flask which is then rotated in an oven at 15 *rpm*. The rotations generate thin films of sample on the inner surface of the vessel. Furthermore, the samples are exposed to air at a constant flow of 4000 *mL/min*. Standard oven temperature and run-time is 163 °C and 5 hours respectively¹⁷.

1.4.2 Long-Term Ageing Processes

Long-Term ageing is the deterioration in rheological properties which, occurs during the asphalt pavements service life and is link to environmental exposure i.e. temperature, sunlight and humidity as well as loading¹⁶. The long-term ageing behaviour is dominated by oxidation in the form of thermal- and photo-oxidation respectively. Since, the temperatures are usually low during the service life of asphalt, very little volatization occurs¹⁷. Most long-term ageing methods work by increasing the amount of asphalt surface exposed to oxygen or accelerating the oxygen's diffusion rate. This can be managed by reducing the film thickness of the sample, using pure oxygen-gas, increasing the pressure and temperature.

1.4.2.1 Pressure Ageing Vessel The in-service ageing of asphalt can be simulated through the Pressure Ageing Vessel (PAV). By exposing the asphalt binder sample to high pressure and temperature the oxidative ageing is sped up by increasing the rate of diffusion of oxygen into the asphalt binder. Thus, allowing a simulation of 7 to 10 years worth of ageing to be conducted in around 20 hours. This standard run time of 20 hours was designed to allow for one test run as well as removal of sample and insertion of a new sample within a 24 hour period. Standard pressure is 2.07 *MPA* (300 *psi*) with temperatures at 90, 100 and 110 °C to reflect cold, moderate and hot climates²⁰.

1.4.2.2 Viennese Ageing Procedure The Viennese Ageing Procedure (VAPro) is a very recently developed oxidative ageing test. Here, the pressure and temperature is kept lower at 0.5 *bar* and 60 °C respectively. Instead the atmosphere during the test is not air, here NO_x-gases and ozone are used. Thus, the oxidizing effects are accelerated²¹. The main drawbacks of the method is a relative lack of testing as well as a requirement of specialty equipment such as an ozone generator. The method is therefore, unavailable to most entrepreneurial firms.

1.4.2.3 Long-Term Oven Tests Oven tests such as the TFOT and Rolling Thin Film Oven Test (RTFOT) are most commonly used to simulate short-term ageing. Since the oven temperatures are usually far higher than the ambient temperature in the asphalt pavements service life, the short-term oven tests would result in too much volatization. When the temperatures are lowered to values closer to ambient temperatures, a longer test time can result in ageing behaviour similar to that of field measured asphalt pavements¹⁷. The most common of the Long-term Oven Tests (LTOT) is the AASHTO R30 standard which recommends an ageing period of 5 days at a temperature of 85 °C. This ageing process can supposedly simulate 7-10 years of ageing in the field. However, a study by Li et al found that the AASHTO R30 conditions could only simulate ageing equivalent to 1 to 2 years in the field. Furthermore, increasing the test-time from 5 days to 10 days in the oven at 85 °C, was found to be less efficient than ageing the sample for 5 days at an increased oven temperature of 95 °C²².

1.4.2.4 UV-Light Exposure Ultraviolet radiation can lead to both volatization and photo-oxidative ageing in asphalt. The latter is believed to have a completely different ageing mechanism compared to thermal-oxidative ageing. Essentially a photon is absorbed with energy larger than the internal bond energy of the molecule. Thus the bond will break and produce a free radical. Wavelengths that produce significant photo-oxidative ageing are in the range of 340-380 *nm*²³. A method for UV-ageing was proposed by Li et al. where the asphalt sample was

irradiated by UV-light with a wavelength center at 360 *nm* and a wavelength of 340-370 *nm*. Irradiation intensity and temperature was kept at 21 *W/m²* and 25 °C²⁴.

1.5 Methods for Evaluating Ageing Behaviours of Asphalt

All asphalt samples that have undergone the ageing method must be further analysed. By reviewing the changes in chemical constituents. Thus, methods from analytical chemistry are very useful to evaluate both the oxidation and volatization. Furthermore, these factors along with thixotropy lead to changes in the mechanical properties of the asphalt. Hence, the most common method for evaluating the ageing of asphalt is to simply perform analyses on aged and non-aged samples. The results then generate indexes, which quantifies the ageing. All indexes will be presented in the subsection for the related method. For example the carbonyl index is mentioned under IR-spectroscopy. The indexes can later be converted into a performance indicator using the equation proposed by Wang et al²⁵:

$$\text{Performance Indicator} = \frac{\text{Parameter of Aged Sample} - \text{Parameter of Unaged Sample}}{\text{Parameter of Unaged Sample}} * 100 \quad (1)$$

Thus, the percentile increase or decrease in the property due to ageing is obtained. All ageing indices in this report will be calculated using equation 1 and presented as an increase or decrease from ageing.

1.5.1 Prall Test

Prall or EU-standard "EN 12697-16" is a rutting test developed in the US to measure the abrasive properties of asphalt mixtures. The test is one of several standard methods for mechanical testing in Sweden. A cylindrically shaped asphalt sample with 30 *mm* height and 100 *mm* diameter is submerged in water at a temperature of 5 °C for 5 hours. The sample is then dried, weighed and put into a chamber with 40 steels balls. A rod rotating at 950 *rpm* accelerate the balls which bounce around in the test chamber, the impacts on the sample lead to rutting. During the 15 minutes it takes to conduct the test, cooling water is run over the asphalt sample at 2*L/min*. Finally, an abrasion value can be determined using the following formula:

$$Abr_A = \frac{M_1 - M_2}{\rho_{bssd}} \quad (2)$$

where Abr_A is the abrasion value in millilitres *ml*, M_1 is the mass of water stored specimen surface dry in air prior to abrasion in grams *g*, M_2 is the mass of water stored specimen surface dry in air after to abrasion in grams *g*, ρ_{bssd} is the bulk density of specimen²⁶.

1.5.2 Cantabro Mass Loss Test

The Cantabro mass loss test (CMLT) is a relatively simple abrasion test used to evaluate the durability of asphalt mixtures as well as an indicator for the bonding properties between the asphalt binder and aggregates²⁷. The ductile behaviour observed in the CMLT is according to Cox et al impacted by air void content, brittleness and binder content. Where, larger air void content lead to poor performance in the CMLT. Whilst increasing the binder content typically improves the ductile performance of the asphalt⁴. Typically, the samples are shaped into cylinders of 65 *mm* height and 100 *mm* diameter. They are then conditioned at 25 °C for several hours and weighed individually. Afterwards the samples are placed in a Los Angeles Abrasion Test drum holding temperature of 25 °C, for 10 minutes spinning at a speed o 30 *rpm*. Dust is brushed off

from the sample, which are then weighed. The Cantabro mass loss (CML) can then be calculated using equation 3:

$$Cantabro\ Mass\ Loss = \frac{m_1 - m_2}{m_2} * 100 \quad (3)$$

where m_1 is the weight of the sample before testing and m_2 is the weight of the sample after testing⁴.

1.5.3 Indirect Tensile Strength Ratio

The ITSr or Indirect tensile ratio is a method for testing the freeze-thaw behaviour of asphalt pavements. Therein, the moisture resistance of the asphalt can be assessed by comparing the tensile strengths of dry samples with that of samples saturated with water. It is generally assumed the water penetrates into the aggregates and therefore pushes out the binder and hinders it from holding the material together, resulting in the material stripping²⁸. Most commonly, the European standard SS-EN12697-12 is used for measuring the ITSr. Herein, two cylindrical sample specimens of equal size and dimensions are prepared. Dry samples are simply stored at 20 °C temperature under ambient atmosphere. Wet samples are submerged in a water bath at an elevated temperature. After conditioning, the indirect tensile strength is measured for both samples at a test temperature which varies depending on the grade of asphalt binder used. The indirect tensile strength ratio (ITSr) is then determined by the ratio of the indirect tensile strength (ITS) of the submerged sample divided by that of the dry sample²⁹. As expressed in equation 4:

$$ITSr = \frac{ITS_{Wet}}{ITS_{Dry}} * 100 \quad (4)$$

where ITS_{Wet} is the indirect tensile strength of the submerged sample and ITS_{Dry} is the indirect tensile strength of the sample conditioned in room temperature under an ambient atmosphere²⁹.

1.5.4 Bulk Density

The European standard SS-EN 12697-6 describes the standardized method for determining the bulk density of an asphalt sample. Meaning how to determine the density of a sample including the air voids at a known temperature. First the sample is weighed in air. The sample is then submerged in water at test temperature for 30 minutes to 3 hours. The sample is then weighed whilst still submerged in water. After which the sample is removed from the water and dried with a towel. It is then weighed for a final time. Lastly, the bulk density can be determined by equation 5:

$$\rho_{bssd} = \frac{m_1}{m_3 - m_2} * \rho_w \quad (5)$$

where ρ_{bssd} is the bulk density measured using the Saturated Surface-Dried method in Mg/m^3 , m_1 is the mass of the dry sample in g , m_2 is the mass of the sample in water in g , m_3 is the mass of the saturated surface dry sample in g , ρ_w is the density of water at test temperature in Mg/m^3 ³⁰.

The density of water is usually determined using equation 6:

$$\rho_w = 1,00025205 + \frac{7,59 * t - 5,32 * t^2}{10^6} \quad (6)$$

where ρ_w is the density of water at test temperature in Mg/m^3 , t is the temperature of the water in degrees Celsius ($^{\circ}C$).

1.5.5 Maximum Density

The maximum density of an asphalt sample is the density of the sample excluding the air voids, measured at a known temperature. Firstly, the dry asphalt sample is placed in a vessel, called a pyknometer, and weighed under ambient atmosphere. The pyknometer is then filled with de-aired and demineralized water which is held at test temperature for at least 30 minutes. Then weigh the submerged sample. Lastly the maximum density can be calculated using equation 7:

$$\rho_{mh} = \frac{m_3 - m_1}{(m_3 - m_1) - (m_4 - m_2)} * \rho_w \quad (7)$$

where ρ_{mh} is the maximum density measured using the Hydrostatic method in Mg/m^3 , m_1 is the mass of the empty pyknometer in air in g , m_2 is the mass of the pyknometer in water in g , m_3 is the mass of the pyknometer and test dry sample in g , m_4 is the mass of the pyknometer and test sample in water in g , ρ_w is the density of water at test temperature in Mg/m^3 calculated from equation 6:³¹

By inputting the bulk and maximum densities into equation 8, the air void content can be calculated:

$$V_a = \frac{\rho_m - \rho_b}{\rho_m} * 100 \quad (8)$$

where ρ_m is the maximum density, ρ_b is the bulk density and V_a is the air void content³².

1.5.6 Softening Point

As the name implies the softening point is a temperature at which, a material flows/softens beyond a specific level under a specific load whilst heated. In the ball and ring method explained in European standard SS-EN 1427; two discs are filled with a bituminous sample which, supports the weight of a 3.5 g steel ball and placed in a beaker. The beaker is placed in a deionized water bath which, is heated following a standardized heating rate until the two balls are fully sunken into the binder and fully coated. At which point the softening temperature is recorded. The softening point is expressed as an average of the softening temperatures of the samples³³.

1.5.7 Infrared Spectroscopy

IR-spectroscopy has become a staple in analytical chemistry due to its usefulness and absence of sample preparation. The technique exposes the sample to light with wavelengths in the infrared region. As the light is absorbed by the sample and raises the internal energy level of the sample by an amount proportional to the energy of the absorbed photon. Thereby causing an increase in either the rotational or vibrational energy of the molecule. Although, a change in dipole moment as the molecule vibrates or rotates is a criteria for absorption³⁴. A spectra can then be constructed as percent transmittance T or absorbance A versus the wavenumber ν . Furthermore, the transmittance can be expressed as the ratio of intensity of transmitted radiation by the sample I to that incident on the sample I_0 . Hence the following equation³⁵:

$$A(\nu) = \log_{10} \frac{I_0}{I} = \log_{10} \frac{100}{T} \quad (9)$$

The spectra can then be compared to frequency charts from IR stored data banks. Since all molecules have characteristic absorption frequencies, the functional groups and finally the entire molecule can be determined³⁴. Furthermore, IR-spectroscopy can be used to evaluate the ageing of asphalts. By creating indexes for a functional group. These indexes are usually defined by the following equations³⁶:

$$I_{CO} = \frac{A_{CO}}{A_{CH_2} + A_{CH_3}} \quad (10)$$

were I_{CO} is the Carbonyl index, A_{CO} is the area under the graph of the carbonyl peak, A_{CH_2} area under the graph of the CH_2 stretch, A_{CH_3} area under the graph of the CH_3 stretch.

$$I_{SO} = \frac{A_{SO}}{A_{CH_2} + A_{CH_3}} \quad (11)$$

were I_{SO} is the Sulfoxide index, A_{SO} is the area under the graph of the sulfoxide peak, A_{CH_2} area under the graph of the CH_2 stretch, A_{CH_3} area under the graph of the CH_3 stretch.

1.5.8 Gel Permeation Chromatography

Whilst Gel Permeation Chromatography (GPC) sometimes called Size Exclusion Chromatography (SEC) is not performed in this thesis work, it will be briefly mentioned for its potential usefulness in asphalt ageing evaluation. The method uses dilute solution of sample which is run through a column containing a porous gel. Since smaller molecules can permeate into the gel, they must take a longer path through the column. Thus, the larger molecules have the shortest elution times as they have the shortest "elution path" as they can permeate into fewer pores, the larger the molecular size. This way the contents of small molecules can be detected³⁷. Since, mostly smaller molecules are removed during the volatilization and polymerization processes in asphalt ageing; GPC may be used to quantify the reduction/loss of small molecules due to asphalt ageing²⁵. Although, equipment would likely be accessible through Chalmers facilities, it was considered to time consuming to add another evaluation method to the thesis work. Hence, GPC was excluded from this thesis work to prioritize methods evaluating oxidation.

1.6 Environmental Considerations

In an article by "Ingenjören" magazine, the annual consumption of bitumen for Swedish road-works was estimated to 400 000 tons³⁸. The question then arises; is the current Swedish paper industry sufficient to replace 25 wt% bitumen in asphalt with lignin? To answer the question data on the annual lignin production is necessary. Roughly, 50 000 tons are produced annually in Sweden by one of the major paper and pulping producers alone. Thus, a replacement of 25 wt% bitumen in asphalt with lignin is not necessarily manageable with the current paper industry. The annual lignin yield is however, large enough to substitute 10 % of the bitumen in asphalts. Although, it is unlikely for lignin to replace bitumen at a 1:1 ratio in a properly proportioned asphalt. Furthermore, the replacement of bitumen in asphalt will face future competition from plastics and carbon fiber industries, which are looking to introduce lignin as precursors for their products as well.

Furthermore, the integration of lignin in asphalt will lead to a carbon sink. Currently, lignin is burned for heating and electricity. The burning of lignin currently serves as a heating source in the paper and pulping processes. Thus, using the lignin as an additive in asphalt will require an

alternative heating source in the paper and pulp industry. A Life Cycle Assessment by Moretti et al. investigated the environmental of lignin in Dutch asphalts, found that the replacement of 25 % of lignins in conventional asphalts would lead to almost 6 % decrease in green-house gas emissions. Importantly the use of natural-gas as a heating source in the paper and pulp production could lead to a significant increase in greenhouse gas emission. However, alternative heating sources could be compensated by the reduction in environmental impact by the replacement of bitumen in the asphalt³⁹. It can therefore be concluded that an asphalt paving company must consider the environmental impact from their lignin suppliers production when assessing the environmental impact on the new lignin-integrated asphalt.

2 Materials and Method

All aggregates of sizes 0-2 *mm*, 2-4 *mm*, 4-8 *mm* and 8-11 *mm* as well as mineral filler was provided by Peab Asphalt. Similarly bitumen of grade 100/150 was provided by Peab asphalt. Kraft lignin was provided by Peab Asphalt. Dichloromethane was provided by Peab Asphalt.

2.1 Experimental Methods

Overall the method for this study was conducted as follows: three asphalts were proportioned and their gradation curves were plotted using excel. Two lignin-integrated batches of 10 wt% and 25 wt% lignin respectively. Furthermore one reference batch with no integrated lignin was produced. Bitumens and aggregates were preheated at 130 °(C) for 4 hours. Three 40 *kg* asphalt-aggregate mixtures were then mixed in accordance to proportion at an elevated temperature, 130 °(C) for the two lignin batches and 160 °(C) for the reference batch. After mixing each batch was split into to two 20 *kg* halves. One half was sent through the ageing regimen the other was immediately compacted and evaluated. The ageing process used the LTOT. Thus, loose-mix asphalt was placed on a number of trays inside a heating cabinet at 95 °(C) for 7 days. The non-aged half simply skipped the ageing step. After ageing the aged asphalt was compacted into 11 Marshall-bodies using 50 stamps, cylindrical test specimens roughly 100 *mm* diameter and 60 *mm* thickness of approximately 1.25 *kg*. The Marshall bodies were then distributed for the mechanical testing. Two Marshall bodies were used in the Prall test, three in the Cantabro Mass Loss Test and six in ITSR.

A non-compacted amount bitumen-aggregate mixture of roughly 1.5 *kg* from each batch was cleaned with dichloromethane. The dichloromethane-bitumen solution was separated in a roto-evaporator in order to yield bitumen for the softening point tests and FTIR. The aggregates were put through a sieve which separates the aggregates into its courses. A gradation curve is then produced to verify the aggregate content in the asphalt mix with the proportioning. Furthermore, bulk and maximum density measurements both used 600 *grams* each.

Softening Point measurements and all mechanical tests were conducted in accordance to the Europeans Standards as described in documentation by SIS - Swedish Standards Institute. Brief descriptions as well as the European standard can be found in Section 1.5.

2.1.1 Proportioning and Mix Gradation Curves

All three batches produced are SMA-11 100/150 asphalts. Meaning stone mastic asphalts with the largest aggregate size of 11 *mm* using a bitumen of penetration grade 100/150, minimum penetration 10 *mm* and maximum penetration 15 *mm*. The proportioning was conducted using Peab asphalts software in which, the mix gradation forms a plot of percentage vs sieve size (*mm*). This plot can be compared with the limits from the Swedish Transport Administration to evaluate if the proposed mix is approved for the mix type e.g. SMA-11. From the proportioning the masses of each grade needed can easily be calculated by multiplying the percentage with the total with of the asphalt batch. Only the proportion from the reference will be presented in this report. See Figure 5 for a mix gradation of the reference represented by the results from the particle size distribution of the aggregates by sieving, determined using the method described in European standard SS-EN 12697-2. The main differences between the reference batch and the lignin-integrated batches is the substitution of bitumen at a 1:1 by mass ratio with lignin. In the 10 wt% lignin batch the 10 wt% bitumen was replaced. Otherwise, the aggregate distribution was kept as similar as possible between the two batches. However, in the 25 wt% lignin batch the 25 wt% bitumen was replaced. Furthermore, to accommodate for the low amount of binder, the 4-8 *mm* grade was omitted. This was motivated by this aggregate grade soaking up a large amount of binder. The rest of the aggregate grades were kept as close to the distribution in the

reference batch as possible.

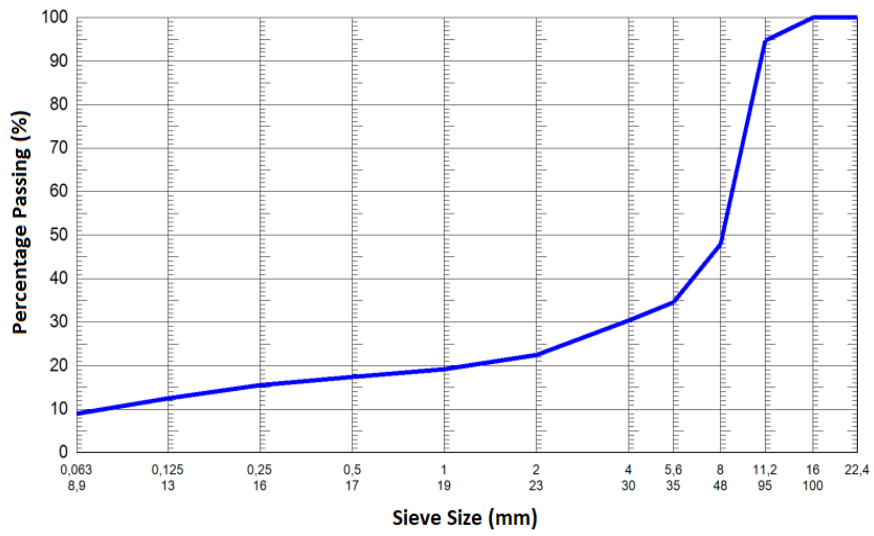


Figure 5: Mix gradation of the SMA-11 100/150 asphalt. The curve describes the aggregate composition of the non-aged reference batch

3 Result and Discussion

In this section the selection of experimental parameters for the ageing method as well as the selection of mechanical tests will be motivated. Furthermore, the results and analysis for each of the mechanical and evaluation tests will be presented below.

3.1 Selection of Ageing Method and Test Parameters

Since this thesis work was commissioned by an entrepreneurial firm; the investigated ageing process must be immediately applicable for industry. As a major goal of this thesis is to introduce an ageing method for the asphalt industry, equipment and facilities at Chalmers University of Technology should be utilized to as little an extent as possible. Hence, the main limitation for the ageing method is simplicity and availability. Whilst, the method of first performing short-term ageing in a TFOT or RTFOT followed by long-term ageing using a PAV appears to be the most common method in academic research papers. The need for the rather specialized equipment of a PAV makes the method inaccessible to most entrepreneurial firms. Similarly, the VAPro method requires an ozone generator which, is unlikely accessible to paving companies. Furthermore the VAPro requires a relatively complicated setup with many components. Any method with few steps and easy setup would be preferable. Furthermore, the possibility of using e.g. a PAV from Chalmers as a method of evaluation by comparison was not possible.

Hence, the LTOT was chosen as the method for simulating the ageing behaviour of asphalt pavements. Ovens and heat cabinets are readily accessible to entrepreneurial firms and are very easy to use. Most commonly the AASHTO R30 standard would be used wherein asphalt is short-term aged for 2h at 163 °C followed by long-term ageing for 120h (5 days) at 85 °C. For this thesis no method for short-term ageing was performed, since short-term ageing is mostly used for simulating the ageing of asphalt binders during mixing and paving. Instead the ageing behaviour of the mixing and paving of the asphalt mixture was simulated by the mixing methodology. Here the bitumen was preheated at 130 °C for the lignin batches and 160 °C for the reference, for 4h in a heat cabinet prior to mixing. Furthermore, the long-term ageing parameters were changed from the AASHTO R30 standard. Instead, the samples were aged for 7 days at 95 °C. This was motivated by the results from Li et al where oven ageing at elevated temperature would lead to more oxidation the higher the temperature and the longer the ageing time. Although the temperature should not exceed 100 °C since the mechanism for oxidation of the asphalt samples at temperatures above 100 °C would differ from the mechanism for asphalt in the field. Furthermore, increasing the time from 5 days to 10 days would lead to an increase in ageing and oxidation. The effect would however, follow the law of diminishing returns. Hence, the increase in time would not lead to an increase in ageing worth the extra cost in energy and time. Thus, 95 °C was chosen as the optimal ageing temperature and 7 days of ageing was chosen for gaining some additional oxidation as well as for ease of performance. A laboratory worker can therefore begin the ageing experiments on e.g. a Thursday and remove the samples from the oven on the following Thursday.

Whats more loose mix ageing followed by stamping of Marshall samples was chosen, rather than ageing the Marshall samples. This choice is motivated by surface area. Since the loose mix asphalt has a larger surface area compared to the compacted Marshall bodies, the loose mix asphalt should be subjected to more contact with the air and therefore heat more easily and most importantly more readily react with the oxygen and lead to more ageing through oxidation. It should however, be mentioned that the ageing displayed in loose mix asphalt will be more uniform compared to field samples. Since, only the surface of the asphalt is in contact with the weathers e.g. sun, rain, air etc. the ageing in the field is non-uniform with a clear gradient. Here the ageing is the most intense at the surface and the level of ageing is reduced deeper into the asphalt pavement. Hence, ageing the Marshall bodies could better simulate the field ageing behaviour

as they are more closely compacted. Although, ageing from the sides would also occur. Many studies from journal articles have solved that problem by using metal sleeves around the Marshall samples. Thus, only the top of the Marshall body is in direct contact with the air. Although, ageing Marshall samples would better simulate the field ageing behaviour of asphalt, the ageing of loose mix asphalt was ultimately chosen. This study is of course interested in simulating the field ageing behaviour of asphalt. Explaining the difference in ageing behaviour between conventional and lignin-integrated asphalt is of higher priority. Hence, the loose mix ageing was chosen since it causes more severe ageing in the asphalt, whilst being sufficiently close to the field ageing behaviour. A follow-up study investigating the ageing method using Marshall bodies could be of interest. Furthermore, ageing loose-mix asphalts reduces the problem of air void contents. Since, greater air void contents increase the permeability of oxygen into the asphalt sample. The air void contents between Marshall stamped batches would be a consideration for the degree of ageing per batch.

Whilst, most ovens distribute heat differently and therefore lead to a difference in optimal ageing time between laboratories, only one set of ageing parameters were evaluated. The possibility of evaluating the chosen parameters of ageing at 95 °C for 7 days as well as 5 days would have been interesting and beneficial. It would however, be impractical. Since only one thesis worker was available for this thesis work; an increase to double the amount of samples for mechanical testing and FTIR and therefore twice the amount of data to analyze would be difficult during a time period of 20 weeks. Therefore, any excess time would be better spent evaluating an additional batch of asphalt with a different lignin content.

3.2 Selection of Methods for Mechanical Testing and Evaluation of Ageing Behaviour

The evaluation methods in this study will fall under two categories. Methods that evaluate the performance of the asphalt and methods that indicate as well as quantify the degree of ageing in the asphalt sample. Infrared spectroscopy will be the primary evaluation tool for the verification and to a lesser extent quantification of ageing. Since oxidation and volatilization are the primary ageing mechanisms, they will both show up in the molecular structure. Hence, intensities and shifts at key functional groups will provide great indications for the oxidation. Primarily from the carbonyl and sulfoxide stretchings. Furthermore, volatilized compounds should lead to absence or decrease of intensity for the corresponding peaks in the FTIR spectra. Whilst, other instruments such as H-NMR, X-ray diffraction and Ultraviolet spectroscopy can provide similar information, FTIR was chosen due to its simple sample preparation and accessibility. Furthermore, the indications for changes in molecular structure from the ageing may also provide a basis for the evaluation in other methods. The softening point measurements are linked to internal energy and forces. Studies do suggest that SARA fractions transition towards the more polar fractions when subjected to ageing through oxidation. Hence, a higher softening point coupled with the results from FTIR may sufficiently verify the ageing of the asphalt samples.

Prall, Cantabro and ITSR were chosen to evaluate the performance of the asphalt. Whilst, these tests could be substituted for other options, they were selected since they are standardized tests recommended by the Swedish Transport Administration. Hence, these tests are reproducible and the equipment necessary should be available at all Swedish entrepreneurial firms. Furthermore, together they provide a versatile analysis on the mechanical properties of the asphalt samples. Information on the resistance to abrasion from the Prall test, tensile strength from ITSR and disintegration resistance from the Cantabro test can together provide an overview on the resilience on not only the asphalt-aggregate mixture. But also on the asphalt mortars durability.

3.3 Experimental Results

All results from the mechanical tests and spectroscopy will be found in the section below. The results from each test before and after ageing will be presented and discussed. A summary of the findings will be presented in section 4 Conclusion.

3.3.1 Infrared Spectroscopy

Bitumen from the asphalt mixes were reclaimed after mixing. In order to separate the bitumen from the aggregates it was dissolved with dichloromethane. A rotary evaporator was then used to separate the bitumen from the solvent. The question was then whether or not the lignin would also be dissolved in the dichloromethane and thus, pollute the bitumen sample. When investigating the FTIR spectra for the reference batch as seen in Figure 6; peaks corresponding to the expected functional groups are displayed. Namely, the peaks at 2920 cm^{-1} and 2850 cm^{-1} are both C-H stretches from alkanes, 1600 cm^{-1} is C=O stretch from carbonyl, 1460 cm^{-1} is a C-H stretch from methyl group, 1375 cm^{-1} is a C-H stretch from aldehyde.

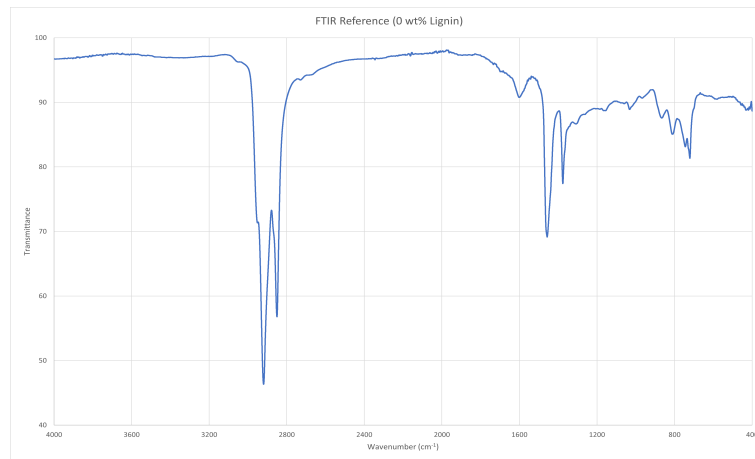


Figure 6: FTIR spectra for recovered asphalt binder from the reference batch. Peaks from functional groups are: 2920 cm^{-1} and 2850 cm^{-1} are both C-H stretches from alkanes, 1600 cm^{-1} is C=O stretch from carbonyl, 1460 cm^{-1} is a C-H stretch from methyl group, 1375 cm^{-1} is a C-H stretch from aldehyde.

When comparing the results for the reference batch with the results for the 25 wt% lignin batch, the spectra are virtually the same. As seen in Figure 7 the same peaks are shown. Although, some differences in intensity are present.

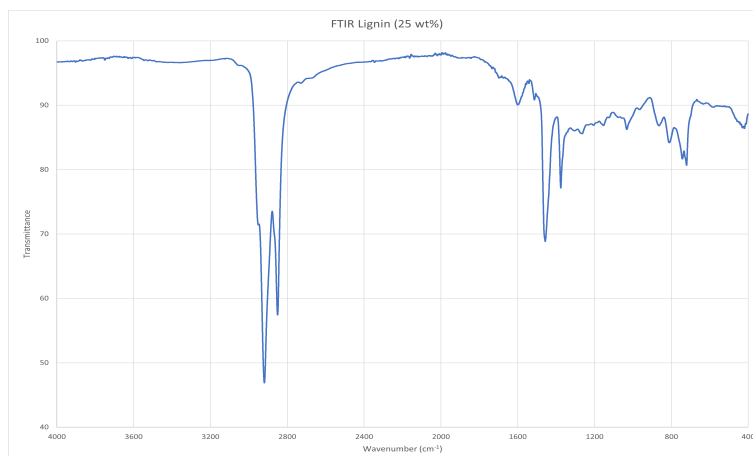


Figure 7: FTIR spectra for recovered asphalt binder from the 25 wt % lignin batch. Peaks from functional groups are: 2920 cm^{-1} and 2850 cm^{-1} are both C-H stretches from alkanes, 1600 cm^{-1} is C=O stretch from carbonyl, 1460 cm^{-1} is a C-H stretch from methyl group, 1375 cm^{-1} is a C-H stretch from aldehyde, 1033 is a S=O stretch from sulfoxide.

Furthermore, the spectra for the 10 wt% lignin batch displays the same peaks as the other two. By investigating Figure 8 all peaks are found. The only differences seen are differences in intensity.

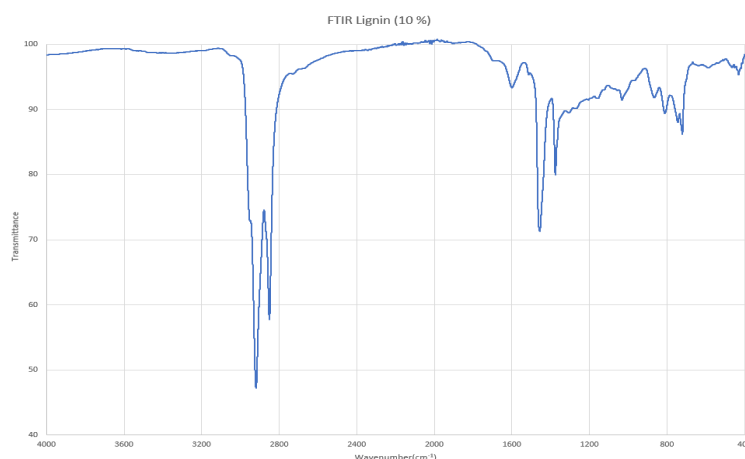


Figure 8: FTIR spectra for recovered asphalt binder from the reference batch. Peaks from functional groups are: 2920 cm^{-1} and 2850 cm^{-1} are both C-H stretches from alkanes, 1600 cm^{-1} is C=O stretch from carbonyl, 1457 cm^{-1} is a C-H stretch from methyl group, 1376 cm^{-1} is a C-H stretch from aldehyde, 1032 is a S=O stretch from sulfoxide.

Considering that all three spectra for the non-aged bitumen samples display the same peaks, it can be interpreted as the spectra displaying the same molecule. Which, they practically do, considering they are bitumen from the same production batch. Whilst, the differences in intensity may be interpreted as the local structure surrounding the functional group is different, this does not necessarily mean lignin is present in the 25 wt% and 10 wt% lignin spectra. The bitumen was pre-heated in a heating cabinet prior to mixing the asphalt batches with the temperatures of the reference batch at $160\text{ }^{\circ}\text{C}$ and the 25 wt% and 10 wt% lignin batches at $130\text{ }^{\circ}\text{C}$. Thus, the differences in intensities between the spectra are more likely related to volatilization in the bitumen samples. The bitumen used in the reference sample should have been subjected to more volatilization compared to the 25 wt% and 10 wt% lignin batches. Thus, having been short-term aged to a somewhat higher degree.

After ageing; the same recovery procedures were conducted on the asphalt samples. Small amounts of bitumen from the aged batches was reclaimed and then analysed using FTIR. Spectra

for the aged reference as well as 25 wt% and 10 wt% lignin batches are displayed in Figures 9, 10 and 11, respectively. All peaks corresponding to the functional groups found in the the non-aged samples, can also be found in the spectra for the aged samples.

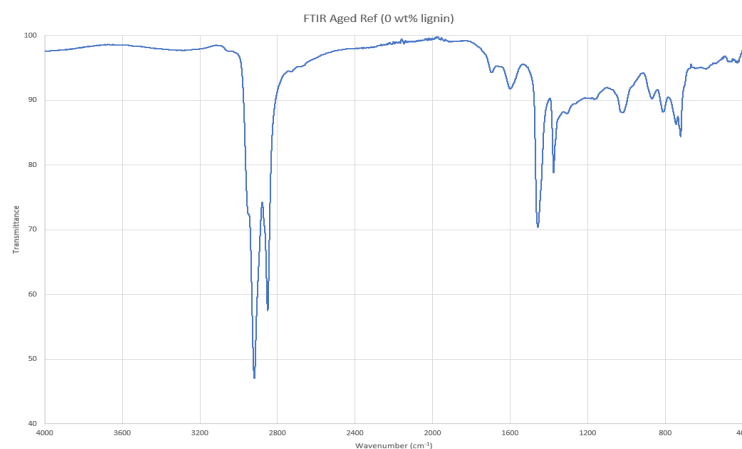


Figure 9: FTIR spectra for recovered asphalt binder from the aged reference batch. Peaks from functional groups are: 2919 cm^{-1} and 2851 cm^{-1} are both C-H stretches from alkanes, 1692 cm^{-1} is a C=O stretching from carboxylic, 1600 cm^{-1} is C=O stretch from carbonyl, 1457 cm^{-1} is a C-H stretch from methyl group, 1376 cm^{-1} is a C-H stretch from aldehyde, 1019 is a S=O stretch from sulfoxide.

Shifts at various peaks have been observed by comparing the spectra in Figures 6 and 9. Although, the C-H stretches at 2920 cm^{-1} and 2850 cm^{-1} have shifted by 1 cm^{-1} after ageing, it is unlikely due to oxidation. More, likely due to measurement error. The most significant differences in the spectra for the reference batch are the emergence of pronounced peaks at 1020 and 1692 cm^{-1} respectively. These peaks are indicative of S=O and C=O stretches respectively. Thus, the FTIR measurement can verify the proposed ageing behaviour in which, the asphalt binder is oxidized by oxygen from the air. The incorporation of oxygen into the asphalt binder can be seen in the significant increases in intensities for the C=O and S=O stretches respectively.

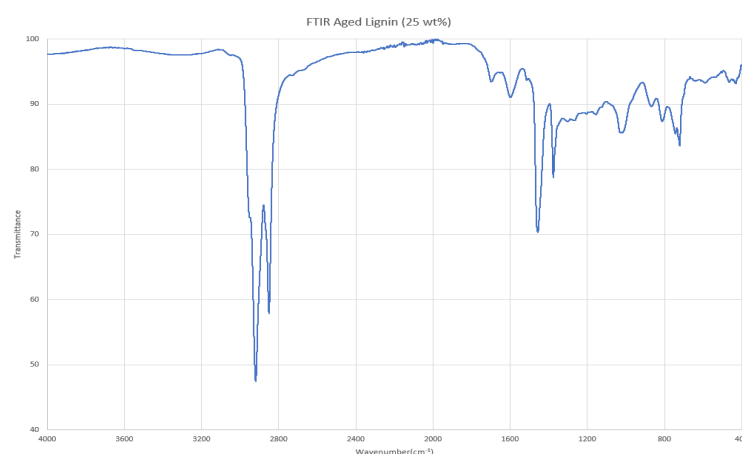


Figure 10: FTIR spectra for recovered asphalt binder from the reference batch. Peaks from functional groups are: 2920 cm^{-1} and 2850 cm^{-1} are both C-H stretches from alkanes, 1696 cm^{-1} is a C=O stretching from carboxylic acid, 1596 cm^{-1} is C=O stretch from carbonyl, 1457 cm^{-1} is a C-H stretch from methyl group, 1376 cm^{-1} is a C-H stretch from aldehyde, 1020 is a S=O stretch from sulfoxide.

By comparing Figures 7 and 10, some shifts may be observed. Firstly, the alkene C-H stretches are identical before and after ageing. Thus, the oxidation does not occur by H^+ as a leaving group. Furthermore, the peaks at 1692 and 1600 cm^{-1} before ageing were shifted to 1696 and 1596 cm^{-1} after ageing, with the peak around 1590 cm^{-1} being significantly more pronounced

after the ageing process. Since both peaks are related to the C=O stretching, they confirm the oxidation of the binder from the ageing method. Similarly, the peak from the S=O stretching is more pronounced and wider after ageing as well as being shifted from 1031 cm^{-1} before ageing to 1016 cm^{-1} after ageing. Similar differences from ageing can also be observed in the 10 wt% lignin batch. By observing Table 11 it is immediately evident the peaks corresponding to the carbonyl and sulfoxide stretchings have become significantly more pronounced after ageing. Furthermore, slight shifts have occurred on the C-H stretches at 2851 and 1456 cm^{-1} respectively. Although, a shift of only 1 cm^{-1} is most likely due to measurement error.

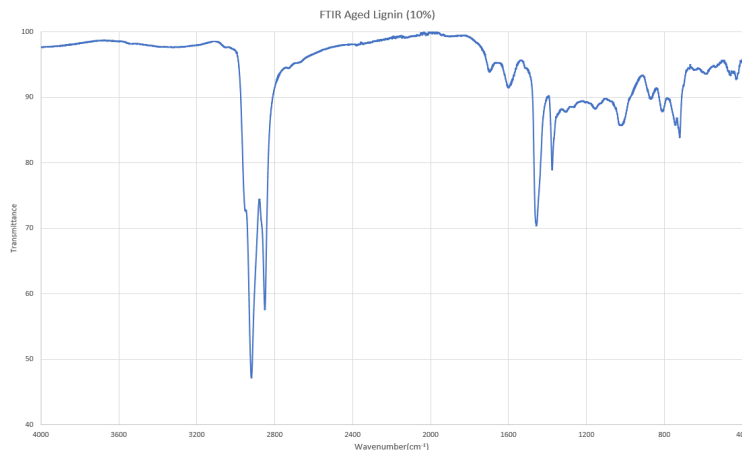


Figure 11: FTIR spectra for recovered asphalt binder from the reference batch. Peaks from functional groups are: 2920 cm^{-1} and 2851 cm^{-1} are both C-H stretches from alkanes, 1698 cm^{-1} is a C=O stretching from carboxylic acid, 1598 cm^{-1} is C=O stretch from carbonyl, 1456 cm^{-1} is a C-H stretch from methyl group, 1377 cm^{-1} is a C-H stretch from aldehyde, 1021 is a S=O stretch from sulfoxide.

If the peak areas from the FTIR graphs are calculated using the Origin software and put into equation 10 and 11; then the oxidation indexes for the carbonyl and sulfoxide groups can be calculated. Thus, the grade of ageing can be estimated. Naturally, no other reactions are assumed to take place other than the oxidation of the asphalt binder. Furthermore, the rate of volatilization is believed to be insignificant. Take note that the integration limits in Origin has to be manually selected for each peak. Selecting integration limits for the sulfoxide peaks for the non-aged batches was particularly difficult. Thus, the oxidation indexes and by extension the performance indexes should not be considered as conclusive evidence but merely as an indicator.

Sample	Ref	Ref Aged	Lig 25%	Lig 25% Aged	Lig 10%	Lig 10% Aged
Carbonyl Index	0.2144	0.4892	0.2324	0.5401	0.5001	0.6004
Sulphoxide Index	0.3699	0.4922	0.5900	1.0254	0.1222	1.1986

Table 1: Carbonyl and Sulfoxide indexes for bitumens from the reference, 25 wt% and 10 wt % lignin batches. All peak areas were calculated using Origin software.

Oxidation indexes are presented in Table 1. As expected all indexes increase after ageing, since the carbonyl and especially the sulfoxide peaks become more pronounced after oxidation has occurred.

Sample	Reference	Lignin 25 %	Lignin 10 %
Carbonyl Index (%)	128.2	132.4	20.06
Sulfoxide Index (%)	33.06	73.80	880.9

Table 2: Performance indexes for the Carbonyl and Sulfoxide indexes, calculated for bitumens from the reference, 25 wt% and 10 wt % lignin batches. All peak areas were calculated using Origin software.

Based on the performance indicators from the carbonyl and sulfoxide indexes; some hypotheses may be drawn. Based on the sulfoxide indexes of the 25 wt% and 10 wt% lignin batches being significantly larger than the reference's, it may be hypothesized that the lignin does not prevent oxidation on the bitumen's sulphur-containing groups. The carbonyl indexes are less conclusive. However, despite the 25 wt% batch having an index comparable to the reference and therefore, comparable degree of oxidation. The 10 wt% lignin batch having a significantly lower carbonyl index might indicate the lignin might hinder the oxidation on the bitumen's carbonyl groups. However, it is noteworthy that more FTIR measurements must be conducted before a strong conclusion may be drawn. Furthermore, the degree of ageing is not 100 % uniform in the ageing method conducted in this thesis. The top layers of asphalt in each tray will have been aged to a larger degree as it was in greater contact with the air. Since, it is unknown if the bitumen measured in the FTIR were "top" or "bottom" layers whilst aged; the results from FTIR may only serve as indication rather than strong evidence.

3.3.2 Softening Point

The softening points of all three batches were rather similar. As seen in Table 3, the softening points for the non-aged samples were 45.0, 45.2 and 45.0 °C for the reference batch, 25 wt% and 10 wt% lignin batches respectively. After ageing the softening points increased to 57.8, 55.6 and 59.6. However, a power outage did occur during the measurement of the aged reference batch. Therefore, the measurement had to be re-initiated whilst at an elevated temperature. However, any effects on the result are expected to be very minor. Softening points as with transitional temperatures are related to the internal forces of particular compounds. Since, the softening point is the temperature at which a material displays a specific viscosity. It may alternatively be expressed as the temperature at which a material displays a specific resistance for its molecules to move past each other. Stronger intermolecular forces as well as entanglements increase the difficulty for molecules to move in respect to each other. Thus, sufficient energy needs to be added into the system, in order for the molecule to overcome its crosslinks, entanglements and adhesive forces. Factors impacting the softening point are polarity, molecular weight and molecular structure.

Sample	Ref	Ref Aged	Lig 25%	Lig 25% Aged	Lig 10%	Lig 10% Aged
Soft Point(°C)	45.0	57.8	45.2	55.6	45.0	59.6

Table 3: Softening points measured using the ring and ball technique, for the non-aged and aged reference, 25 wt% and 10 wt% lignin samples, respectively.

Since the softening points of all three bitumens have increased after ageing, they can act as indicators that the ageing method has worked as intended. Significant increases in softening points of 28.4 %, 23.0 % and 34.4 % for the the reference and 25 wt% and 10 wt% lignin batches respectively indicates a difference in the chemical structure before and after ageing. This increase can be explained by many factors but they all lead back to enthalpy and entropy. Stronger intermolecular forces and polarity lead to an increase in enthalpy. Meanwhile, increases in molecular weight increase entropy and larger branch chains lead to steric hindrance and thus, lead to reductions in entropy. Given the theoretic mechanisms for ageing in asphalt. Most volatization and therefore mass loss, will occur in the short term step. In this study the short term ageing occurred prior to mixing the binders and aggregates. With the softening points being measured on bitumen separated out of the finished asphalt mix. Thus, only the long term ageing will have an effect on the softening points. The limited volatization during the long term ageing processes would likely bring a smaller mass loss compared to the mass gain from the oxidation reactions. Thus, a net gain in mass will likely occur and contributing a a slightly higher softening point, through increases in Van der Waals and London dispersion forces.

More importantly the oxidation reactions lead to conversions in the SARA fractions where the non-polar fractions of saturates and aromatics are transformed into compounds belonging to the polar resin and asphaltene fractions. Thus, the increases in polarity will increase the enthalpy in the bitumen leading to a higher softening point.

If the performance indicator is calculated using equation 1 for the softening points for both batches then the following result is obtained: the increases in softening points are 28.4 %, 23.0 % and 34.4 % for the the reference and 25 wt% and 10 wt% batches respectively. As expected the 25 wt% lignin integrated batch shows promising "anti-ageing" behaviour. Since kraft lignin can more readily react with oxygen-containing radicals compared to the bitumen, it may explain the lesser degree of ageing displayed by the 25 wt% lignin batch. Furthermore, a single iteration of the experiments is not enough to prove the hypothesis. It does however, indicate a lesser degree of oxidation and ageing on the 25 wt% lignin batch compared to the reference. However, the poor performance of the 10 wt% lignin batch indicates the opposite. Note, that many factors will impact the softening point. Thus, the values for the individual batches cannot quantify the ageing and indicate which batch has best resisted the ageing. The increases in softening points can however, prove that the ageing method has worked and the asphalt binders have oxidized. Furthermore, the softening point measurements indicate an increase in stiffness in all binders. Most, likely the 10 wt% lignin batch is the stiffest after ageing, followed by the reference and with the 25 wt% lignin batch being the least stiff after ageing.

3.3.3 Air Void and Binder Contents

The air void content of an asphalt sample can be measured by inputting the bulk density and maximum density into equation 8. Air void contents in asphalt pavements are linked to mechanical properties. By comparing the results in table 4 a hypothesis can be formed: the batch containing 25 % lignin should likely perform the worst in the Cantabro test due to a larger air void content. Furthermore, the lower binder content in the batch containing 25 % lignin will lead to further decreases in ductility in the CMLT. The difference in binder content between the non-aged and the aged 25 % lignin batches is likely due to uneven mixing. Most of the medium grade was removed in order to allow for more integration of lignin. This was done in order to reduce the amount of binder to the greatest extent possible. Since the aggregate courses display rather large differences in size, it is easier for the smaller aggregates to gather at the bottom of the mixer, once the mixing has stopped. Thus, when the first half of the batch was removed to make up the non-aged batch, most bitumen had likely, gathered lower in the mixer. Therefore, the half which, would be used for ageing had more bitumen gathered. This difference in binder content between non-aged and aged 25 % lignin samples needs to be considered during the mechanical testing. Whats more the binder contents and air void contents between the 10 % lignin and reference batches are comparable. Hence, the integration of lignin should be the main impact on the differences in mechanical resilience.

Sample	Ref	Ref Aged	Lig 25%	L25% Aged	Lig 10%	L10% Aged
Bulk Density	2.443	2.372	2.270	2.248	2.344	2.335
Maximum Density	2.508	2.459	2.452	2.325	2.436	2.440
Air Void Content (%)	2.6	3.5	7.4	3.3	3.8	4.0
Binder Content (%)	5.6	5.9	4.0	5.4	5.2	5.2

Table 4: Bulk and maximum densities as well as air void contents for the non-aged and aged reference, 25 wt% and 10 wt% lignin samples, respectively.

3.3.4 Cantabro Mass Loss Test

By investigating table 5 the Cantabro mass loss for the non-aged asphalt samples can be compared. Notably, the CML is a factor 5 larger for the 25 % lignin samples compared to the reference. This is very much indicative of the air void content which, is 5 %-units larger in the 25 % lignin sample. Furthermore, the binder content in the reference is larger than the batch containing 25 % lignin. The 10 wt% lignin displays a Cantabro loss more comparable with the reference. This is not only due to the air void and binder contents being more similar between the two batches. Whats more the proportioning was kept as similar as possible when designing the 10 wt% lignin batch. Thus, the large CML-values in the 25 wt% batch are likely due to poor proportioning. It is most likely due to the omission of the medium-sized 4-8 *mm* courses. Thus, the most important take away from the Cantabro mass loss test should be the improvement or deterioration after ageing.

Sample	Ref1	Ref2	Ref3	Lig1	Lig2	Lig3	Lig4	Lig5	Lig6
Mass Before (<i>gram</i>)	1207	1206	1199	1192	1239	1223	1197	1210	1205
Mass After (<i>gram</i>)	1170	1175	1159	1029	1072	975.2	1134	1115	1137
Cantabro Loss (%)	3.05	2.58	3.37	13.7	13.5	20.3	5.26	7.84	3.84
Av Cantabro Loss (%)	3.00			15.8			5.65		

Table 5: Results from the Cantabro Mass Loss Test, Ref1-Ref3 for the non-aged reference and Lig1-Lig3 for 25 wt% and Lig4-Lig6 for 10 wt% lignin samples respectively.

As seen in Table 5, the average mass loss in the 25 % lignin batch is roughly 5 times larger than that of the reference batch and almost 3 times greater than the CML of the 10 wt% lignin batch. Importantly it should be noted that the reference batch is a properly proportioned asphalt similar to asphalt pavements used on Scandinavian freeways. This difference in performance between the non-aged samples, therefore indicates that the 25 % lignin batch is rather poorly proportioned. Although, the performance of the 25 wt% lignin batch is very poor, the comparison between non-aged and aged lignin batches can still provide useful information regarding its ageing behaviour. Furthermore, the 10 % lignin batch, which is proportioned as similarly as the reference batch as possible, displays ductility comparable to that of the reference batch. Since, both the lignin integrated batches performed worse than the reference samples, it indicates lignin having a negative effect on the asphalt mortar. The addition of lignin in powdered form may perhaps absorbed an amount of asphalt binder. Thus, reducing the effective binder content. Therefore, leading a weaker asphalt mortar.

Sample	Ref1	Ref2	Ref3	Lig1	Lig2	Lig3	Lig4	Lig5	Lig6
Mass Before (<i>gram</i>)	1188	1221	1220	1227	1215	1226	1221	1200	1211
Mass After (<i>gram</i>)	1144	1161	1167	964.7	1029	962.4	1144	1111	1130
Cantabro Loss (%)	3.72	4.87	4.34	21.4	15.3	21.5	6.30	7.43	6.69
Av Cantabro Loss (%)	4.31			19.4			6.80		

Table 6: Results from the Cantabro Mass Loss Test, Ref1-Ref3 for the aged reference and Lig1-Lig3 for 25 wt% and Lig4-Lig6 for 10 wt% lignin samples respectively.

By investigating Table 6 the performance in the CML after ageing can be assessed. All three batches have deteriorated. After ageing the reference batch still performs the best with a relatively low CML. As in the non-aged tests, the 25 wt% lignin batch is roughly a factor 5 and 3 greater than the reference and 10 wt % lignin batches respectively. As before this poor ductility is related to poor proportioning.

If performance indexes for the CMLT are calculated using equation 1, then the reference sample

has performed the worst. Based on the performance indicators the ductility index from CMLT has deteriorated by 43.7 % for the reference, 22.5 % for the 25 % lignin batch and 20.4 % for the 10 wt% lignin batch. Although, all batches deteriorated after ageing it is hard to say if ageing was the only factor. Most probably the deterioration is due to increased brittleness, caused by the stiffening of the asphalt binder. Notably, both lignin batches deteriorates less than the reference after ageing according to the performance indexes. Lesser deterioration in the lignin-integrated batches could strengthen the hypothesis of the lignin functioning as a radical quencher.

3.3.5 Prall

All three batches of asphalt were evaluated using the Prall test, following the method described by the European Standard SS-EN 12697-16. By investigating Table 7, the reference samples has a significantly lower Prall abrasion value Abr_A compared to the 25 % lignin batch. Hence the reference batch performs significantly better during the Prall test and displays better resistance towards rutting. Furthermore, the 10 wt% lignin batch performed moderately well, displaying better Prall abrasion values than the 25 wt% lignin batch but worse than the reference.

Sample	Ref1	Ref2	Ref3	Ref4	Lig1	Lig2	Lig3	Lig4	Lig5	Lig6	Lig7	Lig8
ρ_{bssd}	2.44	2.44	2.41	2.44	2.26	2.27	2.28	2.27	2.36	2.34	2.33	2.33
Abr_A	15.0	15.5	16.7	18.2	41.7	30.9	29.2	26.6	21.8	24.3	24.8	25.5
Av Abr_A	16.4				32.1				24.0			

Table 7: Results from the Prall Test for the non-aged reference and Lig 1-Lig 4 for 25 wt% and Lig 5-Lig 8 for 10 wt% lignin samples respectively. Bulk densities ρ_{bssd} as well as Prall abrasion values in ml are presented

From Table 7 all Prall abrasion values are displayed for the non-aged batches. Notably the Abr_A for the 25 wt% lignin batch are more scattered than in the other two batches. Sample Lig1 performed particularly poorly, leading to a very large average Abr_A . If the sample is omitted, the Abr_A for the 25 wt% lignin batch is reduced to 28.9. Which, is still significantly worse than the values for the other two batches. Although, the proportion for the 25 wt% lignin batch differs from the other batches, most notably in the omission of the 4-8 mm grade. However, this omission cannot explain the batch's poor abrasion resistance. Since, a report by Dolk found the 4-8 mm grade to only have a minor impact on the performance of asphalts in the Prall tests⁴⁰. The result is most likely due to the large air void content in conjunction with the relatively low binder content in the 25 wt% lignin batch.

Furthermore, the reference has a lower Prall abrasion value than the 10 wt% lignin batch. The major differences between the batches is the slight reduction of binder in the 10 wt% lignin batch besides the addition of lignin. Thus, the worse performance of the 10 wt% lignin batch indicates a correlation between the lignin and a reduction in abrasion resistance. In asphalt pavements the majority of resistance to abrasion originates from the asphalt mortar. The stronger the mortar the stronger the resistance towards abrasion. Furthermore, stronger adhesive properties between asphalt binder and aggregates provides stronger resistance towards abrasion. Thus, the trend amongst the non-aged samples where addition of lignin reduces the Abr_A can be interpreted as the lignin weakening the mortar as well as the adhesion between aggregates and binder.

Sample	Ref1	Ref2	Ref3	Ref4	Lig1	Lig2	Lig3	Lig4	Lig5	Lig6	Lig7	Lig8
ρ_{bssd}	2.36	2.36	2.35	2.36	2.27	2.30	2.29	2.27	2.32	2.33	2.35	2.34
Abr_A	16.7	17.4	19.5	19.1	19.3	20.3	24.1	20.3	21.3	22.0	21.5	24.0
Av Abr_A	18.2				21.0				22.0			

Table 8: Results from the Prall Test for the aged reference and Lig 1-Lig 4 for 25 wt% and Lig 5-Lig 8 for 10 wt% lignin samples respectively. Bulk densities ρ_{bssd} as well as Prall abrasion values in ml are presented.

After undergoing accelerated ageing differences in abrasion resistance are observed and presented in Table 8. As expected the reference deteriorated slightly. Although, the deterioration in Abr_A of 2 ml is rather small. Therefore, the reference can be considered as performing comparatively before and after ageing. Unexpectedly, both the 25 wt% and 10 wt% lignin batches improved their performance after ageing. In the case of the 25 wt% lignin batch the disparity in air void content and binder content between the the aged half and the non-aged half should be considered. As seen in Table 4, the air void content in the non-aged half is 4 %-units larger than in the aged half. Similarly the binder content was 1.4 %-units lesser in the non-aged half compared to the aged half. Thus, a significant part of the "improvement" after ageing should be attributed to the aged half being a "better" asphalt-mix. Although, some improvement likely came from the ageing, since the 10 wt% lignin batch also displayed an improvement in abrasion resistance after ageing. Part of this improvement should be attributed to the increase in binder stiffness from ageing. However, if increased stiffness was the only factor in the improvement of the 10 wt% lignin batch, then the reference should have displayed a similar behaviour. Which, it did not. It must therefore be assumed the effect comes from the lignin itself. In a study by Menapace and Masad; aged bitumen supposedly take on a micro-structure with small microholes¹⁸. Since lignin can associate well with bitumen, it is possible the lignin can fill those micro-holes or allow for the lignin-bitumen mix to take on a more mechanically favourable structure after ageing. Such a hypothesis will require tests with Atomic Force Microscopy or similar tools to verify.

3.3.6 Indirect Tensile Strength Ratio

All samples were assessed following the European SS-EN 12697-12 standard. Unfortunately, there were issues with the machinery whilst conducting the measurements for the non-aged 10 wt% lignin batch. Hence the values for the tensile strengths are incorrect. However, the error is assumed to be constant between all wet and dry samples for the batch. Thus, the indirect tensile strength ratio should still be correct and can therefore be compared with the ratios for the other batches. All results for the non-aged reference, 25 wt% and 10 wt% lignin batches can be found in Table 9.

Sample	Ref1	Ref2	Ref3	Lig1	Lig2	Lig3	Lig4	Lig5	Lig6
ITS Wet (kPa)	1610	1470	1530	1470	1280	1490	254	304	270
ITS Dry (kPa)	1870	1440	1180	1440	1450	1260	274	263	254
Average ITS Wet (kPa)	1540			1410			276		
Average ITS Dry (kPa)	1500			1380			264		
ITSR (%)	103			102			105		

Table 9: Results from ITSR, Ref1-Ref3 for the non-aged reference and Lig1-Lig3 for 25 wt% and Lig4-Lig6 for 10 wt% lignin samples respectively. Data marked red due to faulty equipment. Tensile strength values are incorrect. Equivalent relative error should however, lead to a correct ITSR value.

When comparing the tensile strengths of the non-aged samples, the reference batch displays the strongest maximum stress for both the dry as well as the conditioned sets. This is most likely due to the greater binder content in the sample compared to the 25 wt% lignin batch. Thus, the bitumen film thickness can be assumed to be thinner in the 25 wt% lignin batch, resulting in a material with weaker adhesive forces. However, such a hypothesis would require tensile strengths from the 10 wt % lignin to draw a proper conclusion. Since, the 10 wt% lignin batch also had slightly lower binder content than the reference. Notably, the Marshall bodies stamped for the 25 wt% lignin batches did come out thicker than those of the reference batch. Together with the larger air voids content found in the 25 wt% lignin batch could explain why the tensile strength is lower compared to the reference batch. From ratios the moisture resistance can be assessed. ITSRs of 103 %, 102 % and 105 % for the reference, 25 wt% and 10 wt% lignin batches

respectively. Hence the moisture resistance of the different asphalts are comparable, with the 10 % lignin batch performing slightly worse than the two other batches.

Sample	Ref1	Ref2	Ref3	Lig1	Lig2	Lig3	Lig4	Lig5	Lig6
ITS Wet (<i>kPa</i>)	2140	1990	2200	1350	1890	2100	1770	2160	2250
ITS Dry (<i>kPa</i>)	2510	2330	2230	2150	2970	1910	2270	1850	2160
Average ITS Wet (<i>kPa</i>)	2110			1780			2060		
Average ITS Dry (<i>kPa</i>)	2360			2340			2090		
ITSR (%)	89			76			99		

Table 10: Results from ITSR, Ref1-Ref3 for the aged reference and Lig1-Lig3 for 25 wt% and Lig4-Lig6 for 10 wt% lignin samples respectively.

From Table 10 the results from ITSR of the aged reference, 25 wt% and 10 wt% lignin batches can be found. Both the reference batch and the 25 wt% lignin batch displayed increased tensile strengths after ageing. This can be attributed to the increased stiffness in the binder. Therefore, more load is required to deform the asphalt to the point of fracture. Increasing the maximum load of the material. Although, the 10 wt% lignin batch can't be assessed on the tensile strengths alone. However, the tensile strengths of the 10 wt% lignin batch after ageing show strengths comparable to the two other batches. It is probable the tensile strength of the non-aged 10 wt% lignin batch is in the vicinity of the tensile strengths of the reference and 25 wt% lignin batches. A additional ITSR test must be conducted on a 10 wt% asphalt however, before any conclusions may be drawn.

When comparing the indirect tensile strength ratios, then all three batches displayed a deterioration in moisture resistance after ageing. Notably, the 10 wt% lignin batch deteriorated to an ITSR of 99 %, whilst the reference and 25 wt% lignin batch deteriorated to 89 % and 76 % respectively. When performance indicators are calculated: the reference ITSR has deteriorated by 13.6 %, the 25 wt% lignin batch by 25.5 % and the 10 wt% lignin batch by 5.7 %. Moisture damage of asphalts are typically due to the decrease in adhesive and cohesive interactions within the material. Interestingly, the batches with the most and least respective deterioration after ageing were the two lignin batches. Thus, the lignin cannot be the only factor. An explanation comes from the content of lignin. Since, lignin replaces bitumen at a 1:1 mass-ratio in the proportioning, it is possible the bitumen had been reduced too much in the 25 wt% lignin batch. Thus, resulting in a thinner bitumen film. Thereby leading to a larger degree of stripping (binder separating from the aggregate due to water penetration). The good performance of the 10 wt% lignin batch indicates the lignin having a stiffening effect on the asphalt mortar after heating. Which, is further strengthened by the results in the Prall test where both lignin batches improved after ageing. It is possible the ageing method which has successfully lead to an accelerated ageing behaviour by increasing the rate of oxidation in the binder might also induce structural changes that won't be observed during the milder in-field ageing.

4 Conclusion

From the literature review, the main mechanisms and factors for ageing of asphalt pavements was found out. Furthermore, the most common and effective methods for accelerated ageing of asphalts were reviewed. Thus, an ageing method was designed, which could be implemented practically at most Scandinavian entrepreneurial firms without the requirement of additional equipment or expertise. Therefore, the long-term oven test was selected with a temperature of 95 °(C) for 7 days. Which all three asphalt pavement batches successfully underwent.

From the results in FTIR and softening point, conclusive evidence on the ageing method's efficacy was acquired. In FTIR the shifts on key functional groups and more importantly the rise of carbonyl and sulfoxide functional groups after ageing; provide concrete evidence that oxidation has occurred on the binders in all three asphalt pavement batches. Furthermore, the increase of softening points on all three batches verify the hypothesis of increasing polarities in the binder. Thus, indicating ageing through oxidation.

However, the results from the mechanical testing were less clear-cut. The Cantabro Mass Loss test yielded results that were mostly expected. All three batches deteriorated in regards to their ductility after ageing which, is in line with the theory of an asphalt pavements mechanical strength deterioration when aged. From the performance indicators the lignin-integrated batches seems to have deteriorated to a lesser degree compared to the reference batch. Although, their ductilities were weaker overall. Furthermore, the Prall test lead to interesting results. as expected the reference's resistance to abrasion deteriorated after ageing. However both lignin-integrated batches displayed an improvement. Whats more the Indirect Tensile Strength Ratio test lead to more interesting results. The reference and 25 wt % lignin batches both showed deterioration's in moisture susceptibility. Whilst, the 10 wt% lignin batch improved after ageing. This result in conjunction with the improvements from the Prall test may indicate the lignin leading to a more mechanically favourable structure in the bitumen, after the heating from the ageing method. However, such a hypothesis requires verification using e.g. atomic Force Microscopy or Scanning Electron Microscopy.

4.1 Further Research

A few proposals for further research are presented in the list below. The items are in no particular order of importance.

- Optimize the proportioning for lignin-integrated batches.
- Develop an ageing method with UV. A paper by Menapace found a strong interaction between temperature and UV-light on the effect of ageing in asphalts¹⁸. Thus, a method which takes both factors into account should theoretically produce results closer to in-field ageing.
- Investigate the effect ageing has on the micro-structure in the asphalt binder using ATM or SEM. Thus, the unexpected results from the Prall and ITSR tests can be verified and possibly explained.
- Investigate the impact of ageing on aged Marshall bodies. Thus, the ageing method will be closer to ageing in-field and yield an ageing gradient; where the surface is aged to a large degree with diminishing degree of ageing deeper into the asphalt.
- Perform a SARA analysis on the asphalt samples. Thus, the effects on the SARA fractions due to ageing can be evaluated.

References

- [1] Jiantao Wu, Quan Liu, Chonghui Wang, Wenjuan Wu, and Weipeng Han. “Investigation of lignin as an alternative extender of bitumen for asphalt pavements”. In: *Journal of Cleaner Production* 283 (Feb. 2021), p. 124663. ISSN: 09596526. DOI: 10.1016/j.jclepro.2020.124663.
- [2] Joana Peralta, Mohamed Abdel Raouf, Sheng Tang, and R. Christopher Williams. “Bio-Renewable Asphalt Modifiers and Asphalt Substitutes”. In: 2012, pp. 89–115. DOI: 10.1007/978-1-4471-2324-8{_}6.
- [3] Lönn Lundbäck. *Bygg- och anläggningssektorn*. 2018. URL: <https://fossilfritt.sverige.se/roadmap/bygg-och-anlaggningssektorn/>.
- [4] Ben C. Cox, Braden T. Smith, Isaac L. Howard, and Robert S. James. “State of Knowledge for Cantabro Testing of Dense Graded Asphalt”. In: *Journal of Materials in Civil Engineering* 29.10 (Oct. 2017). ISSN: 0899-1561. DOI: 10.1061/(ASCE)MT.1943-5533.0002020.
- [5] James G. Speight. “Asphalt Technology”. In: *Asphalt Materials Science and Technology*. Elsevier, 2016, pp. 361–408. DOI: 10.1016/B978-0-12-800273-5.00009-X.
- [6] Tao Wang, Jiayu Wang, Xiangdao Hou, and Feipeng Xiao. “Effects of SARA fractions on low temperature properties of asphalt binders”. In: *Road Materials and Pavement Design* 22.3 (Mar. 2021), pp. 539–556. ISSN: 1468-0629. DOI: 10.1080/14680629.2019.1628803.
- [7] Meng Guo, Meichen Liang, Ye Fu, Anand Sreeram, and Amit Bhasin. “Average molecular structure models of unaged asphalt binder fractions”. In: *Materials and Structures* 54.4 (Aug. 2021), p. 173. ISSN: 1359-5997. DOI: 10.1617/s11527-021-01754-2.
- [8] Donald R Dimmel. “Lignin”. In: *AccessScience, McGraw Hill* (2020).
- [9] Aleš Ház, Michal Jablonský, Igor Šurina, František Kačík, Tatiana Bubeníková, and Jaroslav Ďurkovič. “Chemical Composition and Thermal Behavior of Kraft Lignins”. In: *Forests* 10.6 (June 2019), p. 483. ISSN: 1999-4907. DOI: 10.3390/f10060483.
- [10] Fadi S. Chakar and Arthur J. Ragauskas. “Review of current and future softwood kraft lignin process chemistry”. In: *Industrial Crops and Products* 20.2 (Sept. 2004), pp. 131–141. ISSN: 09266690. DOI: 10.1016/j.indcrop.2004.04.016.
- [11] Göran Gellerstedt. “Softwood kraft lignin: Raw material for the future”. In: *Industrial Crops and Products* 77 (Dec. 2015), pp. 845–854. ISSN: 09266690. DOI: 10.1016/j.indcrop.2015.09.040.
- [12] Heiko Lange, Silvia Decina, and Claudia Crestini. “Oxidative upgrade of lignin – Recent routes reviewed”. In: *European Polymer Journal* 49.6 (June 2013), pp. 1151–1173. ISSN: 00143057. DOI: 10.1016/j.eurpolymj.2013.03.002.
- [13] Tongyan Pan. “A first-principles based chemophysical environment for studying lignins as an asphalt antioxidant”. In: *Construction and Building Materials* 36 (Nov. 2012), pp. 654–664. ISSN: 09500618. DOI: 10.1016/j.conbuildmat.2012.06.012.
- [14] Adel R. Kakroodi and Mohini Sain. “Lignin-Reinforced Rubber Composites”. In: *Lignin in Polymer Composites*. Elsevier, 2016, pp. 195–206. DOI: 10.1016/B978-0-323-35565-0.00010-2.
- [15] Henglong Zhang, Zihao Chen, Chongzheng Zhu, and Chuanwen Wei. “An innovative and smart road construction material: thermochromic asphalt binder”. In: *New Materials in Civil Engineering*. Elsevier, 2020, pp. 691–716. DOI: 10.1016/B978-0-12-818961-0.00022-3.
- [16] Okan Sirin, Dalim K. Paul, and Emad Kassem. “State of the Art Study on Aging of Asphalt Mixtures and Use of Antioxidant Additives”. In: *Advances in Civil Engineering* 2018 (2018), pp. 1–18. ISSN: 1687-8086. DOI: 10.1155/2018/3428961.

- [17] G.D. Airey. “State of the Art Report on Ageing Test Methods for Bituminous Pavement Materials”. In: *International Journal of Pavement Engineering* 4.3 (Sept. 2003), pp. 165–176. ISSN: 1029-8436. DOI: 10.1080/1029843042000198568.
- [18] ILARIA MENAPACE and EYAD MASAD. “Evolution of the microstructure of unmodified and polymer modified asphalt binders with aging in an accelerated weathering tester”. In: *Journal of Microscopy* 263.3 (Sept. 2016), pp. 341–356. ISSN: 00222720. DOI: 10.1111/jmi.12405.
- [19] D Mastrofini and M Scarsella. “The application of rheology to the evaluation of bitumen ageing”. In: *Fuel* 79.9 (July 2000), pp. 1005–1015. ISSN: 00162361. DOI: 10.1016/S0016-2361(99)00244-6.
- [20] Hussain U Bahia and David A Anderson. “The Pressure Aging Vessel (PAV): A Test to Simulate Rheological Changes Due to Field Aging”. In: *ASTM Special Technical Publication* 1241 (1995), pp. 67–88.
- [21] Daniel Maschauer, Johannes Mirwald, Bernhard Hofko, and Hinrich Grothe. “Viennese Aging Procedure (VAPro): Adaption for Low-Temperature Testing”. In: 2022, pp. 1933–1939. DOI: 10.1007/978-3-030-46455-4_{_}245.
- [22] X-J Li, Yinyong Li, Jin Li, Yuxiang Shen, Chunhai Zhang, and Jincheng Wei. “Effect of laboratory long-term oven aging on the stiffness of asphalt mixtures”. In: *Construction and Building Materials* 258 (Oct. 2020), p. 120252. ISSN: 09500618. DOI: 10.1016/j.conbuildmat.2020.120252.
- [23] Yuanyuan Li et al. “Review of ultraviolet ageing mechanisms and anti-ageing methods for asphalt binders”. In: *Journal of Road Engineering* 2.2 (June 2022), pp. 137–155. ISSN: 20970498. DOI: 10.1016/j.jreng.2022.04.002.
- [24] Yuanyuan Li et al. “Development mechanism of aging depth of bitumen with increasing UV aging time”. In: *Case Studies in Construction Materials* 17 (Dec. 2022), e01057. ISSN: 22145095. DOI: 10.1016/j.cscm.2022.e01057.
- [25] Feng Wang, Yue Xiao, Peide Cui, Juntao Lin, Mingliang Li, and Zongwu Chen. “Correlation of asphalt performance indicators and aging Degrees: A review”. In: *Construction and Building Materials* 250 (July 2020), p. 118824. ISSN: 09500618. DOI: 10.1016/j.conbuildmat.2020.118824.
- [26] Swedish Standards Institute. *Svensk Standard SS-EN 12697-16:2016*. 2016. URL: <https://www-sis-se.eu1.proxy.openathens.net/produkter/anlaggningsarbete/vagbyggnad/korbana/ssen12697162016/>.
- [27] Yi Zhang et al. “Mechanical Performance Characterization of Lignin-Modified Asphalt Mixture”. In: *Applied Sciences* 10.9 (May 2020), p. 3324. ISSN: 2076-3417. DOI: 10.3390/app10093324.
- [28] I. Aghayan and R. Khafajeh. “Recycling of PET in asphalt concrete”. In: *Use of Recycled Plastics in Eco-efficient Concrete*. Elsevier, 2019, pp. 269–285. DOI: 10.1016/B978-0-08-102676-2.00012-8.
- [29] Swedish Standards Institute. *SVENSK STANDARD SS-EN 12697-12:2018*. 2018. URL: <https://www-sis-se.eu1.proxy.openathens.net/produkter/anlaggningsarbete/vagbyggnad/korbana/ss-en-12697-122018/>.
- [30] Swedish Standards Institute. *SVENSK STANDARD · SS-EN 12697-6:2020*. 2020. URL: <https://www-sis-se.eu1.proxy.openathens.net/produkter/anlaggningsarbete/vagbyggnad/korbana/ss-en-12697-62020/>.
- [31] Swedish Standards Institute. *SVENSK STANDARD · SS-EN 12697-5:2019*. 2019. URL: <https://www-sis-se.eu1.proxy.openathens.net/produkter/anlaggningsarbete/vagbyggnad/korbana/ss-en-12697-52019/>.

- [32] Swedish Standards Institute. *Svensk Standard SS-EN 12697-8:2019*. 2019.
- [33] Swedish Standards Institute. *SVENSK STANDARD · SS-EN 1427:2015*. 2015. URL: <https://www-sis-se.eu1.proxy.openathens.net/produkter/petroleum-och-motsvarande-tekniker/vaxer-bitumen-och-andra-petroleumprodukter/ssen14272015/>.
- [34] Richard Osibanjo, Rachel Curtis, and Lai Zijuan. *Infrared Spectroscopy*. Apr. 2022. URL: [https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_\(Physical_and_Theoretical_Chemistry\)/Spectroscopy/Vibrational_Spectroscopy/Infrared_Spectroscopy/Infrared_Spectroscopy](https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Spectroscopy/Vibrational_Spectroscopy/Infrared_Spectroscopy/Infrared_Spectroscopy).
- [35] Robin S. McDowell. “Infrared spectroscopy”. In: *AccessScience, McGraw Hill*, (Sept. 2018). DOI: 10.1036/1097-8542.344700.
- [36] K.B. Batista et al. “High-temperature, low-temperature and weathering aging performance of lignin modified asphalt binders”. In: *Industrial Crops and Products* 111 (Jan. 2018), pp. 107–116. ISSN: 09266690. DOI: 10.1016/j.indcrop.2017.10.010.
- [37] Anthony R Cooper. “Gel Permeation Chromatography”. In: *AccessScience, McGraw Hill* (Jan. 2020). DOI: 10.1036/1097-8542.283900.
- [38] Anna Nyström. “Lignin från skogen kan ersätta olja i asfalt”. In: *Ingenjören* (Sept. 2021). URL: <https://www.ingenjoren.se/2021/09/24/lignin-fran-skogen-kan-ersatta-olja-i-asfalt/>.
- [39] Christian Moretti et al. “Kraft lignin as a bio-based ingredient for Dutch asphalts: An attributional LCA”. In: *Science of The Total Environment* 806 (Feb. 2022), p. 150316. ISSN: 00489697. DOI: 10.1016/j.scitotenv.2021.150316.
- [40] Henrik Bjurström and Ellen Dolk. *Ballastberoende slitage på asfalt och betong: Provnings enligt Prall*. Tech. rep. 2020.

A Appendix: Calculations

Most of the results from the various mechanical tests were calculated using softwares provided by Peab Asphalt. All such calculations would however be rather straightforward to perform as they are rather simple. The results can be manually calculated by putting the experimental data into the corresponding equations found for each mechanical test method found in 1.5 *Methods for Evaluating the Ageing Behaviour of Asphalt*.

A.1 Calculations for the Cantabro Test

All the calculations for the Cantabro tests were calculated using the Matlab software.

```
clear, clc m11 = 1207.0; m12 = 1205.9; m13 = 1199.2; m21 = 1170.2; m22 = 1174.8; m23 = 1158.8;
```

```
CMLR1 = 100 * (m11 - m21)/m11
```

```
CMLR2 = 100 * (m12 - m22)/m12
```

```
CMLR3 = 100 * (m13 - m23)/m13
```

```
CMLRavg = (CMLR1 + CMLR2 + CMLR3)/3 % Cantabro mass loss for the non-aged Reference samples %% m11 = 1191.6; m12 = 1239.3; m13 = 1223.3; m21 = 1028.8; m22 = 1071.7; m23 = 975.2;
```

```
CMLL1 = 100 * (m11 - m21)/m11 CMLL2 = 100 * (m12 - m22)/m12
```

```
CMLL3 = 100 * (m13 - m23)/m13
```

```
CMLLavg = (CMLL1 + CMLL2 + CMLL3)/3 % Cantabro mass loss for the non-aged 25 wt% Lignin samples %% m11 = 1188.4; m12 = 1220.7; m13 = 1220.4; m21 = 1144.2; m22 = 1161.3; m23 = 1167.4;
```

```
CMLR1 = 100 * (m11 - m21)/m11
```

```
CMLR2 = 100 * (m12 - m22)/m12
```

```
CMLR3 = 100 * (m13 - m23)/m13
```

```
CMLRavgA = (CMLR1 + CMLR2 + CMLR3)/3 % Cantabro mass loss for the aged Reference samples %% m11 = 1226.6; m12 = 1215.3; m13 = 1225.5; m21 = 964.7; m22 = 1029.0; m23 = 962.4;
```

```
CMLL1 = 100 * (m11 - m21)/m11 CMLL2 = 100 * (m12 - m22)/m12
```

```
CMLL3 = 100 * (m13 - m23)/m13
```

```
CMLLavgA = (CMLL1 + CMLL2 + CMLL3)/3 % Cantabro mass loss for the aged 25 wt% Lignin samples %% IL = (CMLLavgA-CMLLavg)/CMLLavg IR = (CMLRavgA-CMLRavg)/CMLRavg IL10 = (6.8-5.65)/5.65
```

A.2 Calculations of the Performance Indicators

```
clear, clc Ref = 45.0; RefAged = 57.8; % Softening points Reference Lig25 = 45.2; LigA25 = 55.6; % Softening points 25 wt% Lignin Lig10 = 45.0; LigA10 = 59.6; % Softening points 10 wt% Lignin
```

```
SoftRef = 100*(RefAged - Ref)/Ref %Performance Indicator SoftLig25 =100*(LigA25 - Lig25)/Lig25 SoftLig10 =100*(LigA10 - Lig10)/Lig10
```

%% PrallRef = 100*(18.2-16.4)/16.4 %Performance Indicator Prall25 = 100*(21-32.1)/32.1
Prall10 = 100*(22-24)/24

%% ITSRRRef = 100*(89-103)/103 %Performance Indicator ITSRR25 = 100*(76-102)/102 ITSRR10
= 100*(99-105)/105

A.3 FTIR

clear, clc %Lig 10 non-aged ACH3 = 8317.335; ACH2 = 5592.76; ACO = 1700.37; ASO = 6957.134;

ISO10 = ASO/(ACH3+ACH2) % Sulfoxide Index ICO10 = ACO/(ACH3+ACH2) % Carbonyl Index

%% %Lig 10 aged ACH3 = 8863.3945; ACH2 = 5312.8935; ACO = 8510.9335; ASO = 16992.3485;

ISO10A = ASO/(ACH3+ACH2) ICO10A = ACO/(ACH3+ACH2)

%% %Lig 25 non-aged ACH3 = 8204.071; ACH2 = 5219.737; ACO = 3119.4115; ASO = 7919.978;

ISO25 = ASO/(ACH3+ACH2) ICO25 = ACO/(ACH3+ACH2)

%% %Lig 25 aged ACH3 = 8276.32; ACH2 = 5660.344; ACO = 7527.781; ASO = 14290.508;

ISO25A = ASO/(ACH3+ACH2) ICO25A = ACO/(ACH3+ACH2)

%% %Ref non-aged ACH3 = 9166.5985; ACH2 = 5410.4085; ACO = 3124.829; ASO = 5391.8525;

ISORef = ASO/(ACH3+ACH2) ICORef = ACO/(ACH3+ACH2)

%% %Ref aged ACH3 = 9040.879; ACH2 = 6828.372; ACO = 7763.3595; ASO = 7811.55;

ISORefA = ASO/(ACH3+ACH2) ICORefA = ACO/(ACH3+ACH2)

%% Perf Indexes PSO10 = 100*(1.1986-0.1222)/0.1222 PCO10 = 100*(0.6004-0.5001)/0.5001

PSO25 = 100*(1.0254-0.59)/0.59 PCO25 = 100*(0.5401-0.2324)/0.2324

PSORef = 100*(0.4922-0.3699)/0.3699 PCORef = 100*(0.4892-0.2144)/0.2144