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16. Abstract

Using sustainable, renewable substances that can be locally-sourced instead of petroleum-based asphalt binders would be better for our environment. Replacing a small portion (maximum of 6%) of asphalt binder with three different types of lignin was investigated to determine its effects on aged and unaged asphalt. Kraft lignin, lignin precipitated from black liquor, and lignin produced from rice hulls using a deep eutectic solvent partially replaced a standard asphalt binder (control) and the four binders were evaluated. All three lignins improved the high temperature grading for both aged and unaged samples compared to the control. Non-recoverable creep compliance values were acceptable for the replaced lignin binders and grade bumping was achieved. Multiple Stress Creep Recovery was improved when standard binder was replaced by the lignins. Adding lignin precipitated from black liquor and lignin produced from rice hulls enhanced binder strain tolerance at 64 °C and improved long-term aging index. Additional investigation of binder with lignin precipitated from black liquor showed improved rut resistance and better cracking resistance compared to the control. Replacing petroleum-based binder with up to 6% of lignin precipitated from black liquor is feasible in asphalt.

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Use of Sustainable Lignin to Enhance Asphalt Binder and Mix Properties

by

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ABSTRACT

Using sustainable, renewable substances that can be locally-sourced instead of petroleum-based asphalt binders would be better for our environment. Replacing a small portion (maximum of 6%) of asphalt binder with three different types of lignin was investigated to determine its effects on aged and unaged asphalt. Kraft lignin, lignin precipitated from black liquor, and lignin produced from rice hulls using a deep eutectic solvent partially replaced a standard asphalt binder (control) and the four binders were evaluated. All three lignins improved the high temperature grading for both aged and unaged samples compared to the control. Non-recoverable creep compliance values were acceptable for the replaced lignin binders and grade bumping was achieved. Multiple Stress Creep Recovery was improved when standard binder was replaced by the lignins. Adding lignin precipitated from black liquor and lignin produced from rice hulls enhanced binder strain tolerance at 64 °C and improved long-term aging index. Additional investigation of binder with lignin precipitated from black liquor showed improved rut resistance and better cracking resistance compared to the control. Replacing petroleum-based binder with up to 6% of lignin precipitated from black liquor is feasible in asphalt.

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IMPLEMENTATION STATEMENT

Louisiana-sourced lignin at a level of 6% can replace asphalt binder while maintaining adequate rutting and cracking resistance in asphalt mixes. Grade bumping can also be achieved with lignin replacement.

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INTRODUCTION

Using non-renewable, limited resources to produce asphalt binder requires energy and generates greenhouse gases [1]. In addition, advances in crude oil refining have decreased the amount of asphalt available for use in asphalt binders, increasing cost [2]. Finding renewable, sustainable materials to replace asphalt binder thus becomes a priority. Lignin is the second most abundant biomass material available on our planet. Using it in asphalt binder would reduce the need for petroleum-based material to be transported to paving sites, since local and sustainable lignin from biomass may be able to replace this fossil fuel derivative. Lignin has gained a considerable amount of attention as a modifier for asphalt because of its potential to enhance rheological properties of the binder. Lignin derived from the pulp and paper industry has been applied in asphalt binders, starting in 1979, but most of the studies have not been conducted until recently [3]. The role of lignin has been investigated as an antioxidant as well as a partial replacement of the asphalt binder in recent years. Improvement of high temperature properties of binder modified with lignin was reported by several researchers, but it came with the compromise with low temperature and intermediate temperature properties [4-6]. At low lignin concentration, binder showed limited improvement in aging resistance whereas, higher concentrations affected binders adversely [7]. However, a completely opposite conclusion was drawn in the study conducted by Hobson et. al (2017) where the action of lignin as an antioxidant was not supported and even the extracted binder was found to be slightly more oxidized [8]. Some researchers have used lignin in the HMA as a partial replacement of the binder up to 25%, but the effect of the lignin in the binder was not examined [8, 9]. These studies did not include the testing of mechanical properties of the lignin modified HMA. In one of the few studies performed with non-Kraft lignin, Sundstrom et al. (1983) reported that ductility decreased with increasing steam-exploded from aspen lignin content of asphalt binder [10]. In the most recently published article, Batista et al. (2018) found that Kraft lignin increased the Brookfield viscosity of binders mainly at 135 °C [11]. Lignin when added in asphalt binders gave a lower carbonyl index and thus a higher weathering aging resistance compared with conventional binder and a content of 4 wt.% of lignin has increased thermal stability of binder after the Rolling Thin Film Oven procedure (RTFO) [11]. Dynamic Shear Rheometer analysis showed that as the lignin content in binder increases, the stiffening increases as well and the corresponding high-temperature performance grade for unaged and RTFO aged samples also improves. Moreover, lignin improved the asphalt's resistance to thermal cracking [11].

The divergent findings on the effects of lignin replacement of asphalt binder point to a need to investigate the rheological properties, as well as mix properties, of lignin modified binder before its use in field application. The contradictory findings may be due to different preparations and sources of the lignins used.

A particular lignin’s physical and chemical behavior will be different depending on the original source and extraction method used [12, 13]. Lignin in untreated biomass is a very high molecular weight polymer generally comprised of three possible monomers: paracoumaryl alcohol (H), coniferyl alcohol (G), and sinapyl alcohol (S). These are incorporated into lignin in the form of phenylpropanoids: p-hydroxyphenyl (H), guaiacyl (G),

and syringyl (S). Lignins from different plant materials have differing proportions of the phenylpropanoids. For example, softwood lignin is almost exclusively guaiacyl (G), while grass-type plants have a mixture of all three. Softwood is generally used in the pulp and paper industry, so the lignin extracted from black liquor will be predominantly guaiacyl (G). As rice is a grass-type plant its lignin contains a mix of all three types.
Since wood has many uses, particularly in construction, using it to obtain lignin may not be an environmentally-conscious choice. Using wastes from food production to obtain lignin would prevent landfilling of these wastes [14, 15]. Rice hulls, which are already transported to processing centers in Louisiana, are not valuable as animal feed because of their high content of inorganic molecules (ash). Rice hulls have what is essentially silica "armor" on their outsides, so they are not useful as either animal feed, or even as compost materials [16]. In the United States, 2 million acres are used for rice production [17].
Obtaining lignin from biomass in an environmentally-friendly way has been a continuing challenge to the pulp and paper industry. The widely-used Kraft process requires caustics and sulfide, while other processes require other sulfur-containing chemicals, acids or high pressure.

An exciting alternative type of lignin separation uses deep eutectic solvents (DES). A eutectic system is a homogeneous mix of two solid-phase chemicals that forms a joint super-lattice at a particular molar ratio, called the eutectic composition. This super-lattice then melts at the eutectic temperature that is lower than the melting points of the individual components. DES are formed by hydrogen bonding of the two components. The term "deep" is used because the melting point curve has a particularly deep crevice at the eutectic point. DES have low volatility and are non-flammable, nontoxic, biocompatible, and biodegradable [18]. They are easily synthesized from obtainable materials at high purities [19]. In addition, DES typically do not inactivate enzymes, making them valuable in biomass conversion [20]. They are not sensitive to water content, making their use more feasible with undried rice hulls [18]. Drying costs can be a substantial portion of pretreatment costs for biomass separation [21].

This work investigates the incorporation of three kinds of lignin from biomass into asphalt binder to determine its effect on the binder's properties. Lignin precipitated from black liquor (B), Kraft lignin that was commercially available (C), and lignin that was produced from rice hulls using DES in the laboratory (L) were added into asphalt binder. Extensive testing of these binders was performed to reveal the enhancements possible with lignin addition.

OBJECTIVE

The objective of the research study was to investigate the quality of asphalt binders with some of the standard binder replaced with three types of lignin, as well as mix properties with lignin added.

SCOPE

Figure 1 describes the scope of this study.

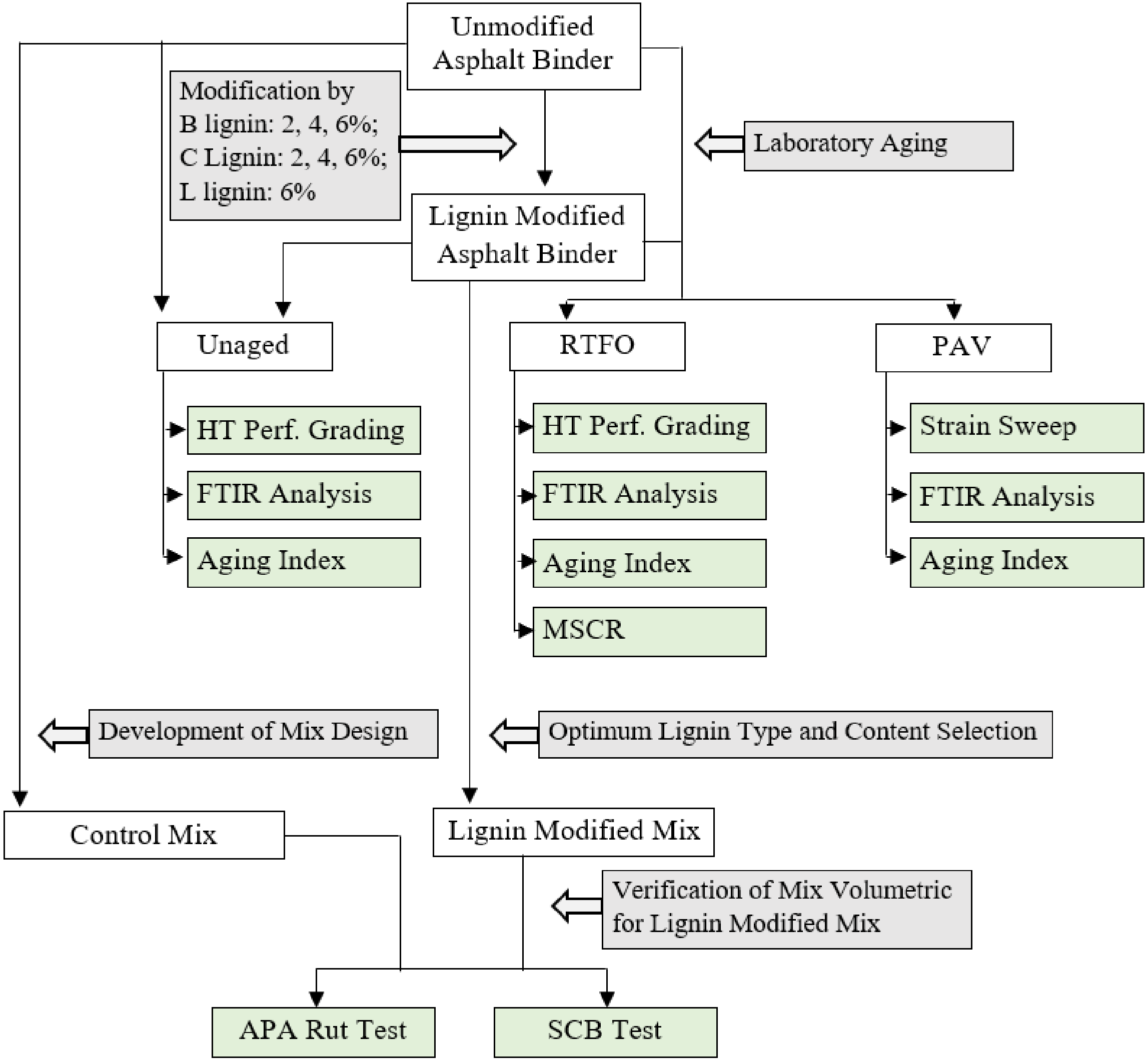


Figure 1: Detailed experimental plan of the study

METHODOLOGY

MATERIALS AND TEST METHODS

Materials:

Rice hulls were harvested in Louisiana and obtained from Falcon rice mill (Crowley, LA, USA). Formic acid was purchased from DudaDiesel (Decatur, AL). Choline Chloride (98%) and sulfuric acid (95-98%) were purchased from Sigma-Aldrich (St, Louis, MO). The commercial lignin (CAS 8068-05-01) was purchased from BOC sciences (Shirley, NY, USA) and is referred to in this work as "C" lignin. The black liquor, from softwood Kraft processing, was kindly supplied by Graphic Packaging International Inc. (Monroe, LA). The black liquor obtained had the following characteristics: pH of 10-12, sodium sulfide 4-8%, sodium hydroxide 4-8%, and sulfates and carbonates 22-27%, cellulose, hemicellulose, and lignin 25-30%. Asphalt binder used for this study was collected from Amethyst Construction, a local asphalt mixing plant in Ruston, LA. The original supplier of the binder is Ergon Asphalt and Emulsion, Inc, Vicksburg, MS. The binder is sold as PG 67-22. High temperature grading of the binder was determined in the laboratory and it was found as PG 68.

Methods:

Procedure for obtaining "L" Lignin from rice hulls:

The rice hulls were dried for 24 h at 105 ˚C and milled to a specific size (mesh 14-28, 1.168-0.589 mm in diameter) before DES pretreatment. The pretreatments were carried out using a biomass concentration of 10 wt% (3 g of dry biomass and 30 g of FA:CC) in a flask that was immersed in an oil bath with magnetic stirring. The pretreatment of biomass with DES was conducted at 155 ˚C for 2 h. The flask was connected to a condenser to precipitate the slightly volatile DES, in order to keep the solvent volume constant. After removal from the oil bath, vacuum filtering with a coarse nylon net filter separated solid biomass residue from DES. The solid biomass was then rinsed with ethanol and separated using the same coarse nylon filter. Following this, DI water was added to the filtrate to precipitate lignin. After precipitation, vacuum filtering with a nylon filter was used to separate the lignin. Additional DI water was used to wash the lignin to increase the purity.

Procedure for obtaining "B" Lignin from black liquor:

The precipitation of lignin fraction through acidification of the black liquor was performed. After heating the black liquor at 60 ˚C, a 6 wt% sulfuric acid solution was added to precipitate the lignin. The precipitated lignin was collected after decantation and washing with additional DI water to remove any water-soluble impurity.

Fourier Transform Infrared (FTIR) Spectroscopy:

A Nicolet IR 100 FTIR (Thermo Scientific, Waltham, MA, USA) with a Diamond crystal using 24 scan per sample was used from 400 to 4000 cm^{-1}. FTIR analysis was performed on both fresh and aged samples, as well as on all different type of lignin, PG-67, and lignins incorporated in PG-67. Binder was heated in a 8 oz tin can on a hot plate at 100 degree Celsius for 20 minutes. When it was enough liquid it was stirred by a spatula and a small drop (5 mm diameter) was poured on a silicone mold. At the time of testing the solid binder drop was placed on top of the diamond crystal of ATR by forceps for FTIR spectroscopy. For pure lignin, powdered sample were used. The advantage of this FTIR technique from a pragmatic point of view is fast and easy interpretation of the spectra for known materials and quick analysis of quality and quantity. All FTIR tests were performed in triplicate to determine the quality and repeatability of the measurements.

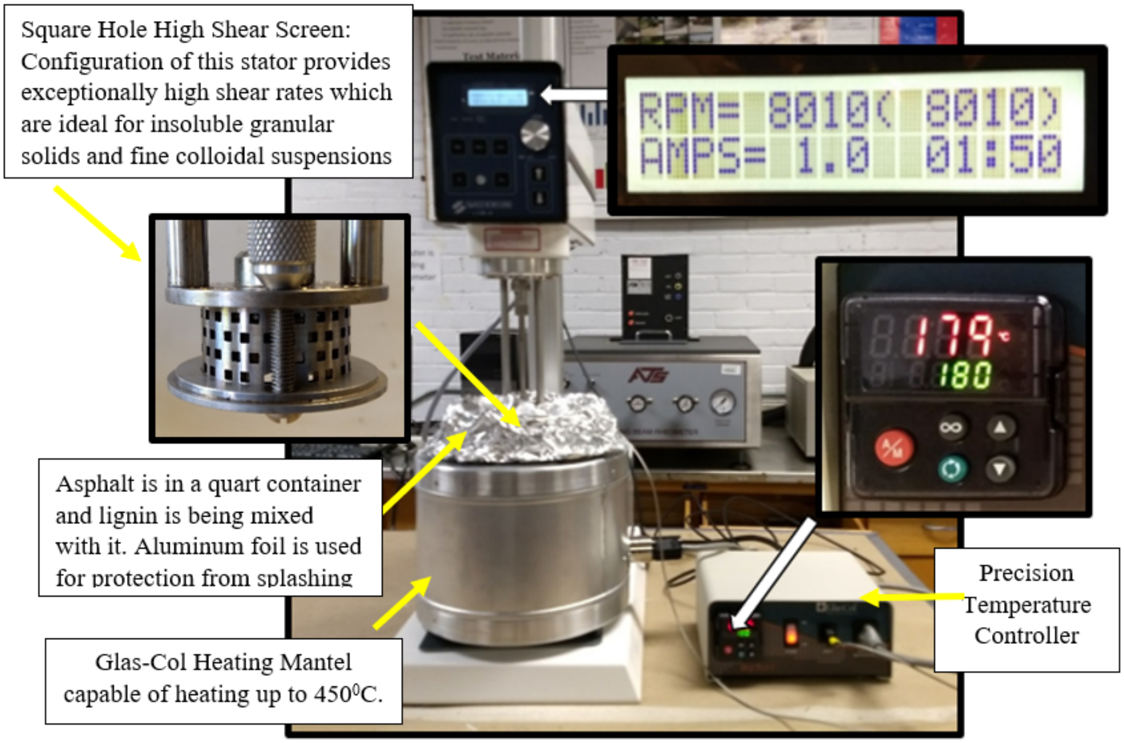
Experimental Plan

Base binder was modified with three types of lignin. Both “B” and “C” were added to base binder at 2%, 4% and 6% while “L” lignin was added at 6% by weight of binder. This study was conducted to investigate the binder properties as well as the behavior of the mix after lignin modification. Neat and modified binders were subjected to short-term and long-term laboratory aging before testing for rheological properties. High temperature performance grading was performed on unaged and short-term aged binder. Percent recovery and non-recoverable creep compliance was determined by multiple stress creep recovery tests on short-term aged binder. Strain tolerance of the long-term aged binder was tested by strain sweep. Aging index was calculated for the unaged, short-term aged, and long-term aged binder based on rheological properties. The above-mentioned tests were performed in a Dynamic Shear Rheometer (DSR). Change in chemical composition because of modification as well as oxidative aging was investigated by utilizing a Fourier Transform Infrared (FTIR) Spectroscopy.

Based on the rheological properties of modified binders, an optimum amount of suitable lignin was selected, and lignin modified Hot Mix Asphalt (HMA) was prepared. In this study 6% of “B” lignin was chosen for mix preparation, due to its good performance and adequate supplies of this material. A laboratory developed mix design was used to make the control and lignin modified mix. An Asphalt Pavement Analyzer (APA) was utilized to determine the rutting resistance of the mixes. Cracking potential of the mix was investigated by a Semi Circular Bend (SCB) test.

Modification of Binder with Lignin

For this study PG 67-22 binder was used as a base binder and three types of lignin were used as modifiers. 500 grams of binder was heated in a quart container at 180 °C in a forced draft oven until it became sufficiently liquid. When it was absolutely flowing, a mechanical mixing blade was inserted into the asphalt and rotational speed was adjusted to make a vortex in the asphalt. The predetermined amount of lignin powder (passing #200 sieve) was then poured slowly into the vortex of the asphalt to promote rapid dispersion without agglomeration. To perform the whole mixing process at a fixed temperature, the container was placed into a heating mantel where the temperature was controlled by a precision temperature controller. The mechanical mixing was continued for five minutes. After that a high shear mixer with a square hole high shear screen was introduced into the binder (Figure 2). Configuration of this stator provides exceptionally high shear rates which are ideal for insoluble granular solids and fine colloidal suspensions. For the first 30 minutes the rotational speed was set at 4000 rpm and for next 30 minutes it was set at 8000 rpm. Volumetric expansion was observed at the beginning of the mixing stage just after the addition of lignin. After 1 hour of blending at 180 °C the lignin seemed to be well mixed with the asphalt. Modified binder was placed into a smaller can and was poured into RTFO bottles immediately after the blending to assure that no lignin settled at the bottom of the quart can.



Square Hole High Shear Screen: Configuration of this stator provides exceptionally high shear rates which are ideal for insoluble granular solids and fine colloidal suspensions

Asphalt is in a quart container and lignin is being mixed with it. Aluminum foil is used for protection from splashing

Glas-Col Heating Mantel capable of heating up to 450⁰C.

Precision Temperature Controller

Figure 2: Blending lignin with base binder using a high shear mixer at elevated temperature

Aging Procedure

Short-term aging of the neat and lignin modified binder was simulated in the laboratory using a Rolling Thin-Film Oven (RTFO) in accordance with AASHTO T 240. RTFO residue was then subjected to accelerated oxidative aging by means of pressurized air at elevated temperature in pressurized aging vessel (PAV) according to AASHTO R 28. RTFO and PAV aged binder along with unaged binder were used for DSR test and FTIR spectroscopy.

Rheological Property Testing

The major objective of the study was to evaluate the improvement of rheological properties of the binder modified with lignin. Different standard rheological tests with little modification of the parameters were conducted using a DSR.

High Temperature Performance Grading. High temperature performance grading of the unaged and RTFO aged binder was performed according to AASHTO T 315. A 25 mm parallel plate and a 1 mm gap were chosen for the test geometry. The test was performed at a 10 rad/sec angular frequency and a 12% strain where temperature was varied from 64 to 82 °C at intervals. The binder was tested for compliance with AASHTO M 320.

Determination of Aging Index. Aging Index (AI) of unaged, RTFO aged and PAV aged binder was determined using a 8 mm plate and a 1 mm gap. Angular frequency and the applied strain was the same as that for the high temperature performance grading test. $G^*/\sin\delta$ parameter was recorded at 64 and 76 °C, which was later used for determination of AI.

MSCR Test. Percent recovery and non-recoverable creep compliance of asphalt binder was determined by means of a multiple stress creep recovery (MSCR) test on RTFO aged binder following the AASHTO TP 70 standard test method. The MSCR test was performed at 64 and 76 °C using a 25 mm plate and a 1 mm gap. The sample was tested in creep at 0.1 kPa and 3.2 kPa stress levels followed by recovery at each stress level. Creep portion of the test lasted for 1 second followed by a 9 second recovery.

Strain Sweep Test. Strain sweeps were performed on PAV aged binder at 64 and 76 °C. Initial and final targeted strains were 1% and 200% respectively. Complex modulus (|G*|) and shear stress were recorded at each applied strain level. The geometry used for this test was an 8 mm plate with a 1 mm gap. This test was performed to determine the strain tolerance of the neat and modified binder.

Mix Design

The asphalt concrete used in this study was designed according to AASHTO R 35 "Standard Practice for Superpave Volumetric Design for Asphalt Mixture." Crushed granite and manufactured sand were used as the aggregate conforming the gradation requirement of table 502-4 of the standard specification. The gradation of aggregate used for this mix is shown in Figure 3. Aggregate were tested for coarse aggregate angularity, fine aggregate angularity, flat and elongated particles and sand equivalency. Optimum asphalt content was determined as 4.6%, according to the table 502-5 of section 502 of the 2006 Louisiana Standard Specifications for Roads and Bridges [22]. Mix was produced at 163 and aged 150 °C for 2 hours in an oven for volumetric calculations. At design gyration of 100, the air void was found 3.89%. Voids in mineral aggregate (VMA) and vds filled with asphalt (VFA) were 13.5% and 69% respectively. The mix passed the resistance to moisture induced damaged performed according to AASHTO T 283 with a Tensile Strength Ratio (TSR) value of 0.86. The loose mix was aged for 4 hours before compaction to test the mechanical property of the mix. The mix was compacted to a targeted air void of 7%, which was reached after 35 gyrations.

Lignin modified mix was produced without altering the gradation or asphalt content. The air void at design gyration was obtained as 4.3%, which is within the specified limit. The mix passed the moisture sensitivity test with a TSR value of 0.80.

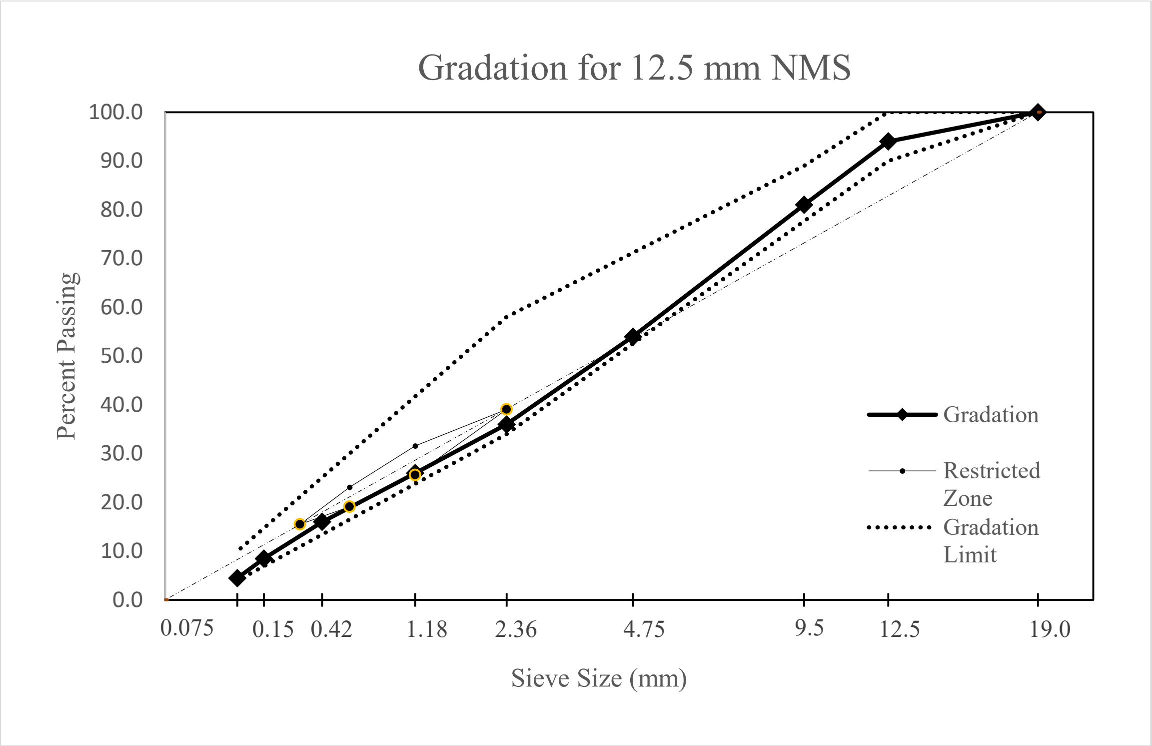


Figure 3: Aggregate gradation for SUPERPAVE mix design

Mix Property Testing

APA Rut Test. Rutting tests were performed on laboratory mix, laboratory compacted specimens. Control and lignin modified mixes were targeted to compact at a 7% air void which was attained at 35 gyrations. A certain amount of mix was taken for compaction so that after 35 gyrations the height of the compacted specimen became 75 mm. APA was used to determine the rut resistance of the mixes. Testing temperature was fixed at 64 °C . The testing was conducted at 100 psi hose pressure and 100 pounds vertical wheel load. Rut depth was measured manually after 8000 cycle wheel-passes.

SCB Test. The Semicircular Bend (SCB) test was performed according to AASHTO TP 124. A 50 mm thick semicircular disk was obtained from a 150 mm diameter gyratory compacted sample with 7% air void. A 15 mm deep notch parallel to the loading axis was cut on the SCB specimen. A load was applied along the vertical radius of the specimen at 50 mm/min rate and the vertical displacement was measured during the entire duration of the test. Using the load-displacement curve different parameters and indices can be computed.

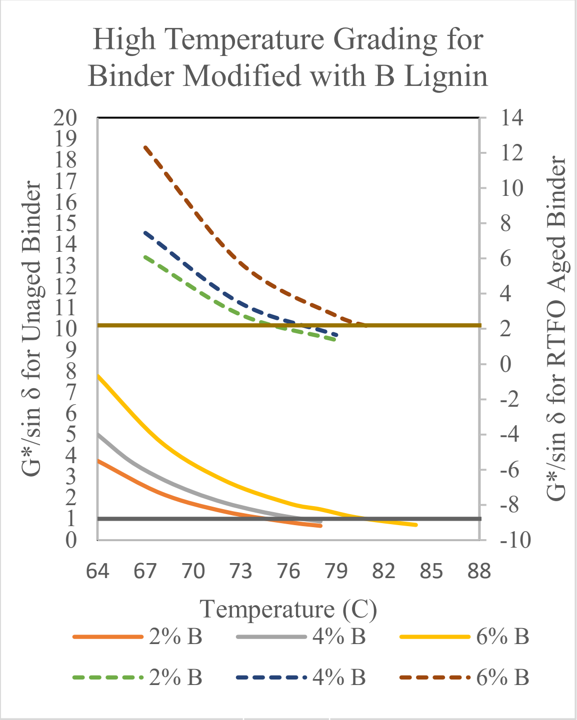
DISCUSSION OF RESULTS

RESULTS AND DISCUSSION

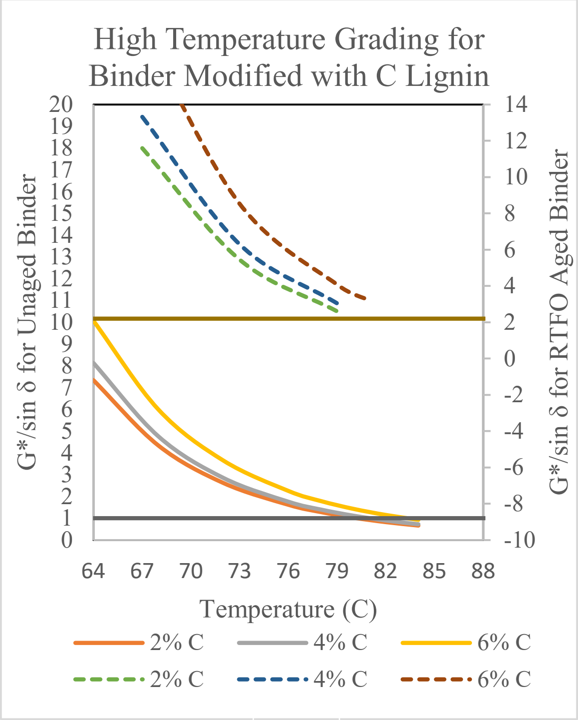
Binder Test Results

High Temperature Grading

By definition, high temperature performance grade of a binder is the maximum temperature in degree Celsius, at which the unaged and RTFO aged binder possesses a G*/sinδ value equal to or above 1.00 kPa and 2.20 kPa respectively. High temperature continuous grading of unaged and aged binder was performed for both neat and modified binder and are plotted in Figure 4(a), 4(b) and 4(c). With increases in the percentage of lignin, the high temperature grade increases irrespective to the types of lignin added. When the same amount of lignin is added, type C lignin is responsible for the most increase in stiffness and type L is responsible for least increase. Figure 4(d) is the plot of high temperature performance grade of the lignin modified binders. It can be noted that, if unaged and RTFO aged binder satisfy the minimum stiffness criteria at slightly different temperature the lower temperature is considered as high temperature performance grade. Modification of lignin significantly improved the high temperature grade of the binder from 68.5 ℃ to at least 74.5 ℃ or some cases up to 82 ℃, which means that modified binder has more stability in high temperature and are more resistant to permanent deformation or rutting.



(a)



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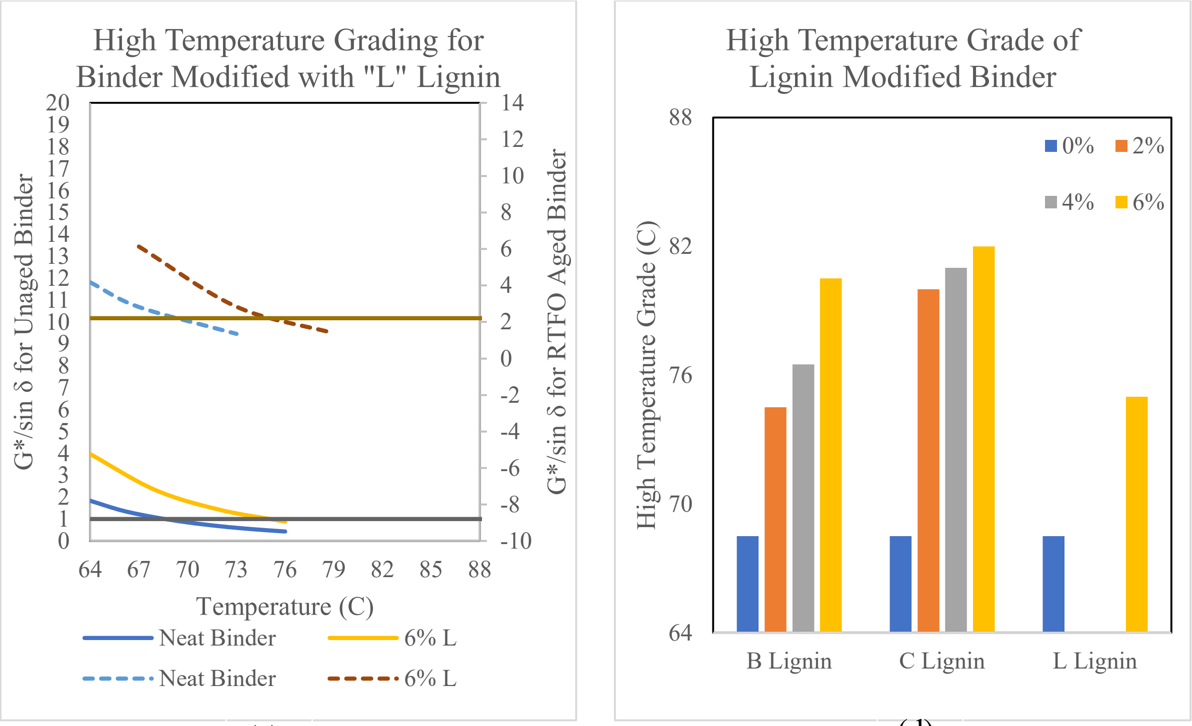


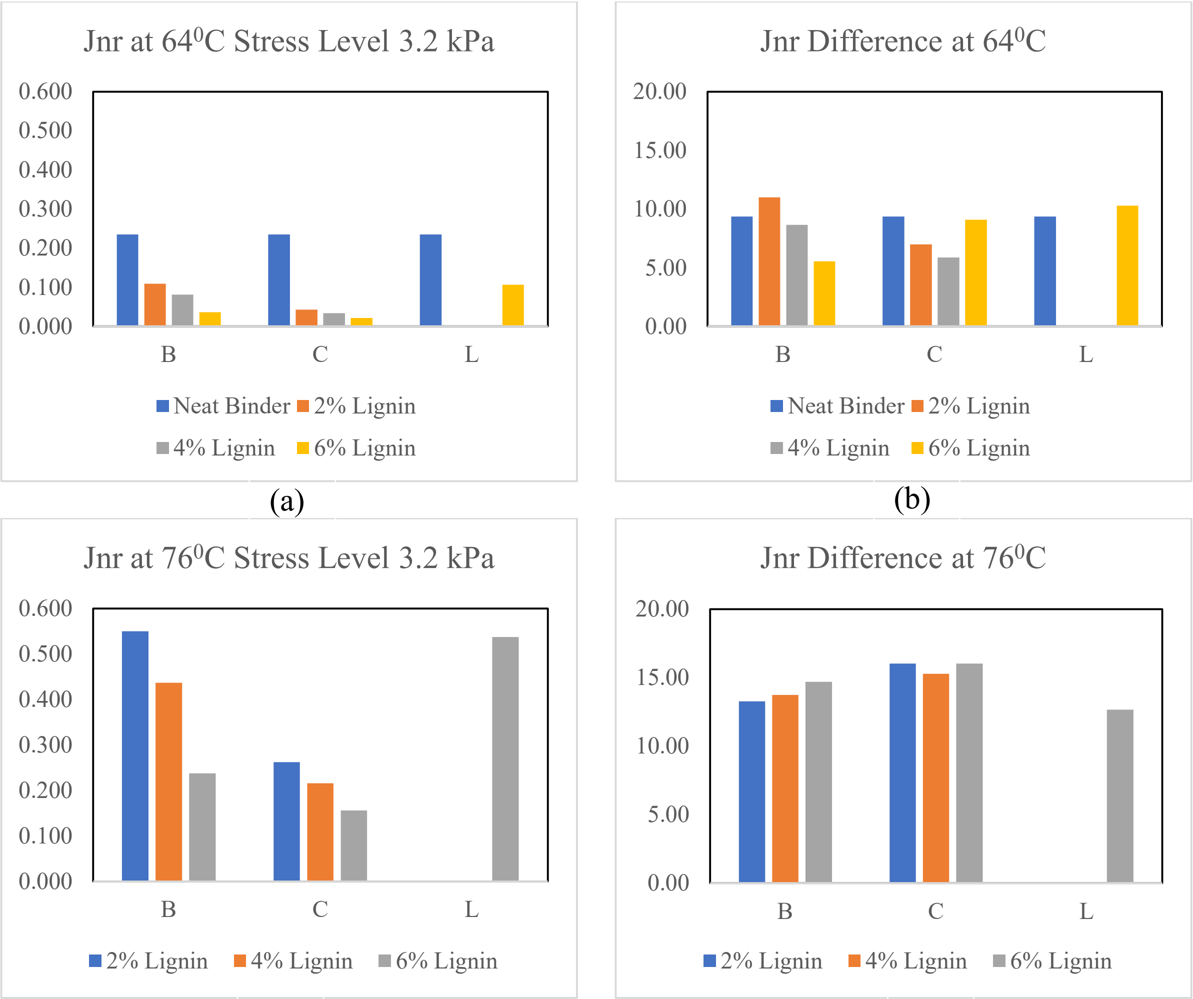
(c) (d)

Figure 4: High temperature performance grading of the neat and modified binder

Grading According to Vehicular Loading Condition

Performance grading of asphalt according to vehicular loading condition was performed in accordance with AASHTO MP 19. Asphalt binder is classified into four categories: Standard grade (S), High grade (H), Very high grade (V) and Extremely high grade (E) based on the non-recoverable creep compliance (J_{nr}) value. The original binder was graded as “E” at 64 °C as it has a Jnr value less than 0.5 kPa^{-1} when tested under 3.2 kPa stress level. At this temperature all the modified binders have the Jnr value way below the maximum limit (Figure 5(a)). After the modification as the high temperature performance grade was improved, the MSCR test was also performed at 76 ˚C. At this temperature all the modified binders were graded as “H” except the binder modified with 6% “L” lignin which was graded as V”. When the binder was modified with B or C lignin, with the increase in lignin amount J_{nr} value decreases but as low as 2% lignin is enough to pass the binder as “E” grade Figure 5(c).

A pavement can be subjected to wide variation of loading during entire service life. From performance point of view, a binder with lower sensitivity against the applied stress is more desirable. Non-recoverable creep compliance of a binder is determined in MSCR test at two stress levels: 0.1 kPa and 3.2 kPa, where responses of the binder are observed when they are under and beyond the linear viscoelastic range respectively. J_{nrdiff} is a parameter which express the percent difference in J_{nr} value calculated at these stress levels. Figure 5(b) and 5(d) shows the Jn_{rdiff} of all the binders at 64 °C and 76 °C respectively. The maximum J_{nrdiff} is observed at 16% which is way below 75%, the maximum allowable value specified by the specification.



(a) (b)

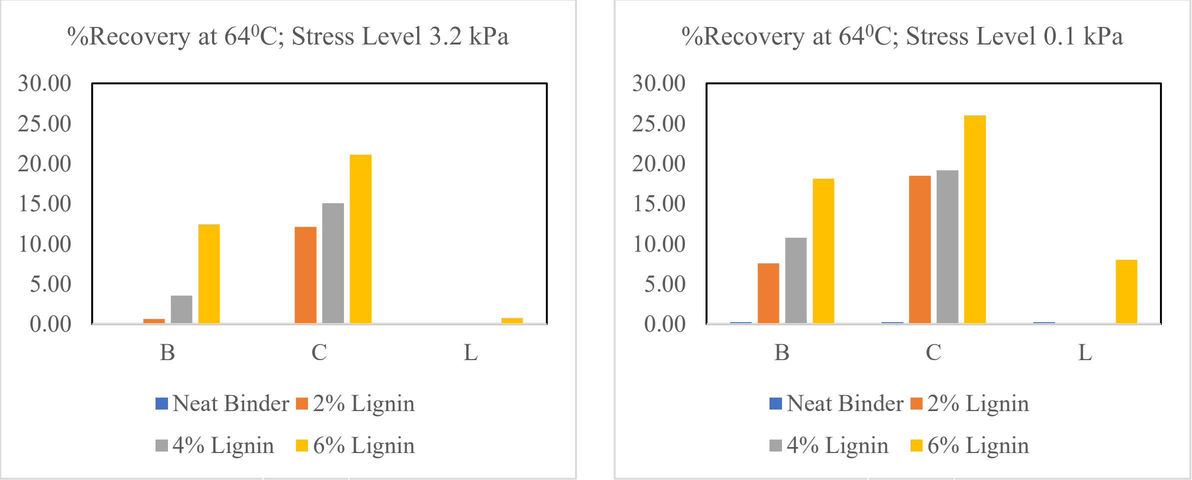
(c) (d)

Figure 5: Non-recoverable creep compliance results from MSCR test

Multiple Stress Creep Recovery Test Results

Modification of binder with elastomeric polymers inhibits the binder from accumulating permanent deformation because of delayed elasticity [23]. As a result, a significant portion of deformation is recovered after the removal of the applied load. The MSCR test measures the recoverable portion of the strain in terms of percent recovery (R) and non-recoverable portion in terms of non-recoverable creep compliance (J_{nr}). Percent recovery of unmodified and modified binders at 64 °C are plotted in Figure 6(a) and 6(b) for applied stress levels of 3.2 kPa and 0.1 kPa. Unmodified binder does not have any recoverable portion of the strain at this temperature under either applied stress level whereas, modified binder exhibits up to 26% and 21% recovery at 0.1 kPa and 3.2 kPa stress level. Binder modified with type C lignin possesses the most percent recovery while type L possesses the least. For the same type of lignin, an increase in added amount increases the percent recovery of the binder.

At 76 °C and 3.2 kPa stress level not a single sample exhibits any recovery while at 0.1 kPa stress level maximum 8% recovery is observed for binder modified with 6% C lignin (plot is not provided here). Modification of binder with lignin increases the stability of the binder at high temperature but the modification is not as effective as the conventional (for example SBS) polymer modification in terms of percent recovery according to AASHTO MP 19.



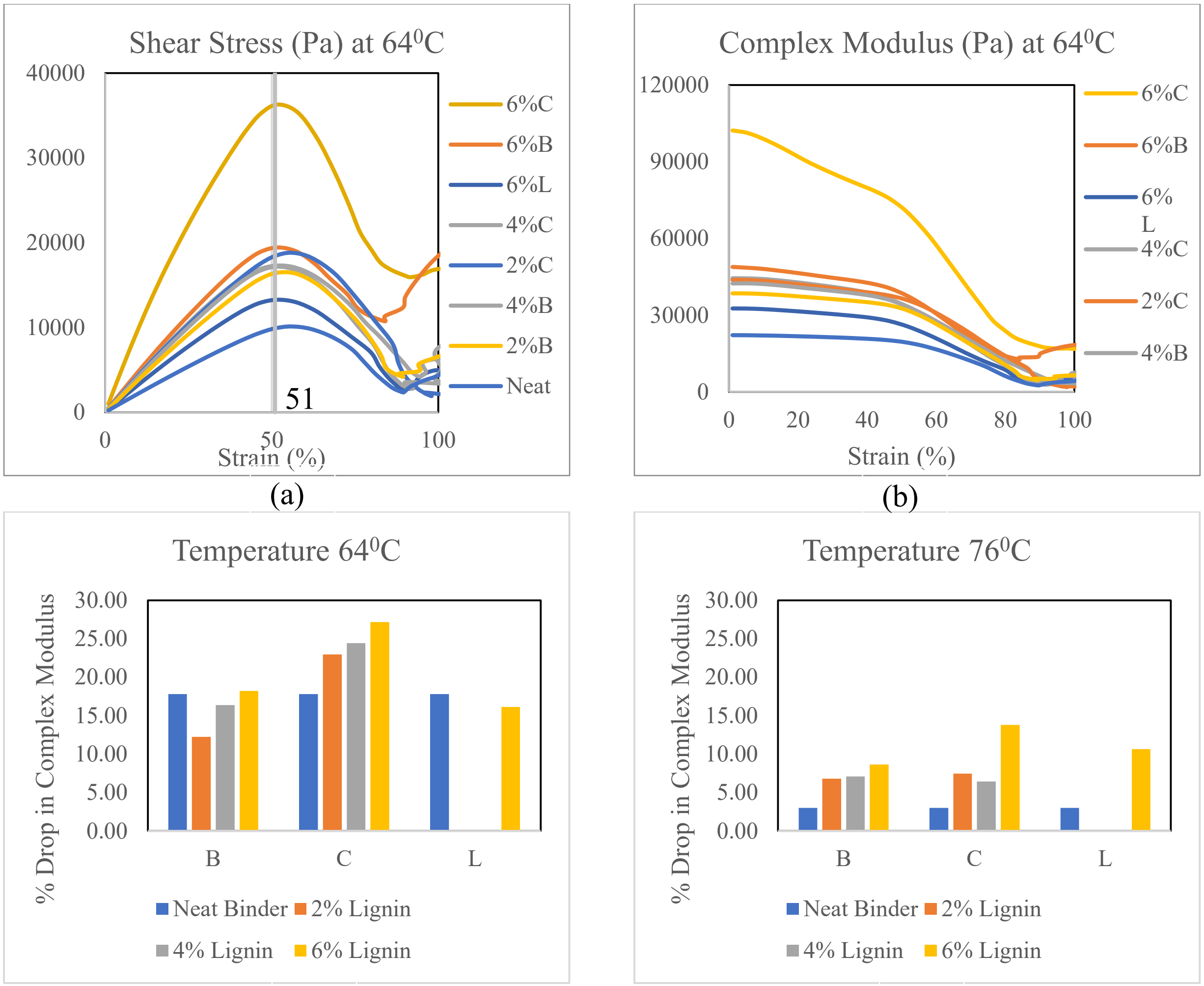
(a) (b)

Figure 6: Percent recovery from MSCR test

Analysis of Strain Sweep Data

In this study strain sweep test data was utilized to evaluate strain tolerance by the drop in complex modulus from initial value and was expressed as percent of initial complex modulus. Lower drop in complex modulus means higher strain tolerance which indicates that the binder is capable of withstanding more strain before failure and vice versa [24]. Figure 7(a) shows the complex modulus results with change in applied strain at 64 °C. It was critical to decide which strain value should be considered to record the initial and final value of complex modulus to calculate the modulus drop. From the Stress-Strain plot of the binder at 64 °C (Figure 7(b)) it is observed that peak shear stress occurs at a certain strain after which the shear stress plummeted. The strain corresponding to peak shear stress is slightly different for individual binders but not less than 51%. So, to calculate the strain tolerance of the binder, complex modulus was considered at 1% and 51% stain as initial and final value respectively. Figure 7(c) is the plot of percent drop in complex modulus of neat and modified binders at 64 °C. Increment of the lignin percent in the binder causes higher drop in modulus, which is true for all types of lignin. Among the three types of lignin, "C" makes the binder less strain tolerant. Except the binder modified with 6% "B" lignin, all other binders modified with B and L lignin show the modulus drop less than the unmodified binder which is an indication of effective binder modification.

Figure 7(d) is the similar plot of modulus drop at 76 °C. At 76 °C the drop in the modulus is lower than the drop at 64 °C because at higher temperature binders become more strain tolerant. But drop in modulus for lignin modified binder is higher than unmodified binder irrespective to modifier type or amount. 76 °C is a much higher temperature than the unmodified binder grade but is close to or even lower than modified binder grade. So, the higher percent drop in modulus for modified binder does not necessarily infer the ineffective binder modification.



(a)

(b)

(c)

(d)

Figure 7: Strain sweep test results

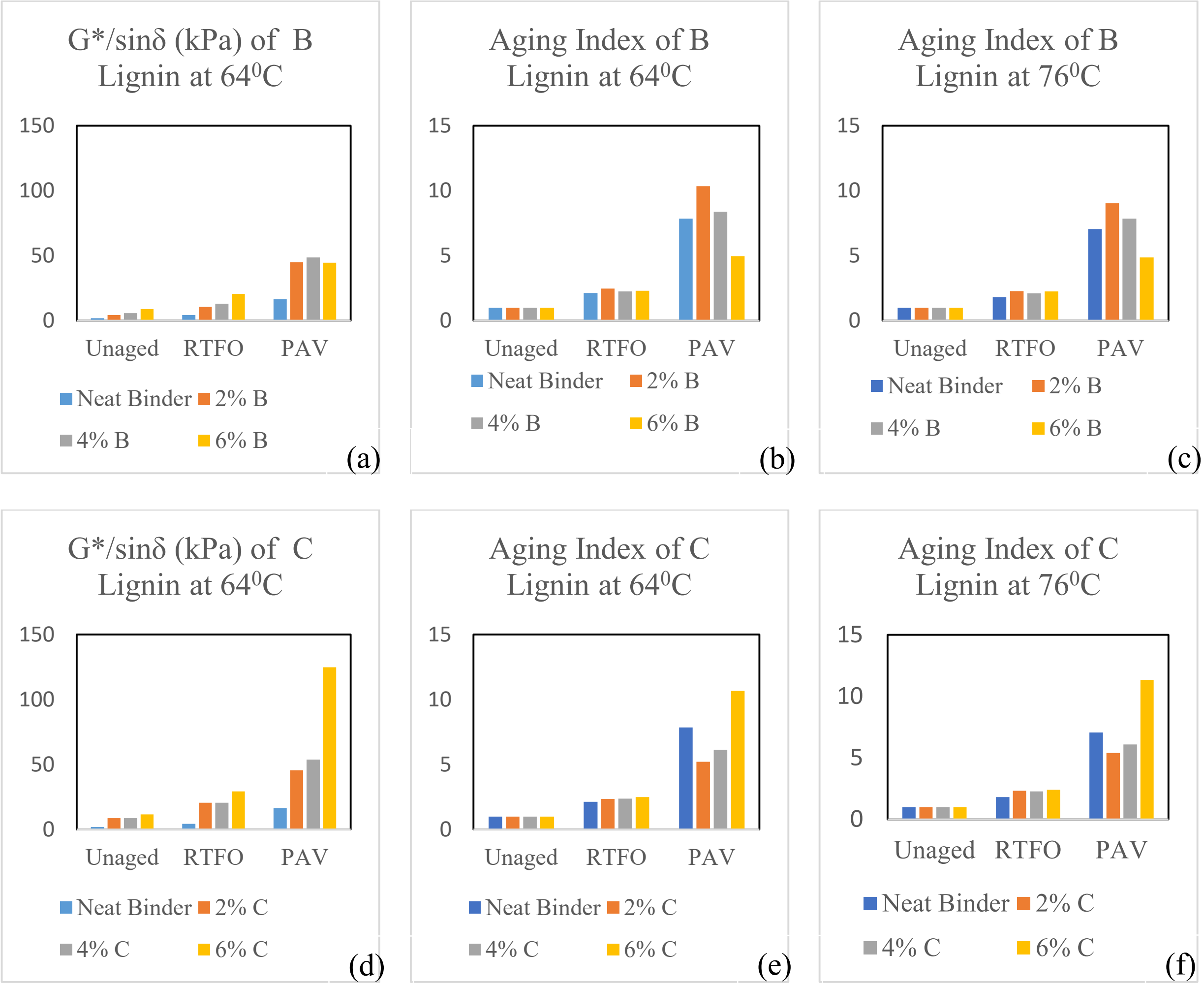
Improvement in Aging Index

Aging index (AI) of a binder is defined as the ratio of stiffness (G*/sinδ) of aged to unaged binder. According to definition stated here, unaged binder has AI of 1.00. A binder with higher aging index implies that it is more susceptible to aging and vice versa. In this study, AI of short-term aged (RTFO aged) and long-term aged (PAV aged) binder was investigated. AI of binder modified with different percent of "B" lignin is plotted in Figure 8(b) for both RTFO and PAV aged binders. RTFO aged binders have slightly higher AI than that of unmodified binder for any amount of added lignin. When 2% B lignin is added the AI after long term aging becomes higher than the unmodified binder but with increase of lignin percent the AI decreases. When a binder is modified with "B" lignin, the stiffness of unaged binder increases with increased amount of added lignin (Figure 8(a)). But after the PAV aging the difference in stiffness among the three modified binders is less pronounced as a result of a higher amount of lignin causing lower AI.

In case of "C" lignin RTFO aged binder has a similar nature of AI but PAV aged binder behaves completely opposite (Figure 8(e)). Increase in lignin amount increases the AI of PAV aged binder. Binder modified with 2 and 4% lignin has lower AI compared to the unmodified binder but addition of 6% lignin results to a much higher AI which is not desirable. Unlike the “B” lignin modified binder, stiffness of “C” lignin modified binder kept increasing after PAV aging with increase of added lignin which causes the increasing trend of AI for “C” lignin modified binder (Figure 8(d)). This result confirms that a higher amount of C lignin is not desirable as a modifier.

Figure 8(g) shows the AI of binder modified with maximum percentage of three different types of lignin. From this Figure it is observed that “B” lignin can cause the lower AI among different types of lignin even lower than the unmodified binder.

From the Figure 8(c), 8(f) and 8(h) it can be observed that at 76 °C, irrespective of lignin type and amount, the trend of change in AI remains the same with almost the same AI value,



indicating that AI is not very sensitive to the testing temperature.

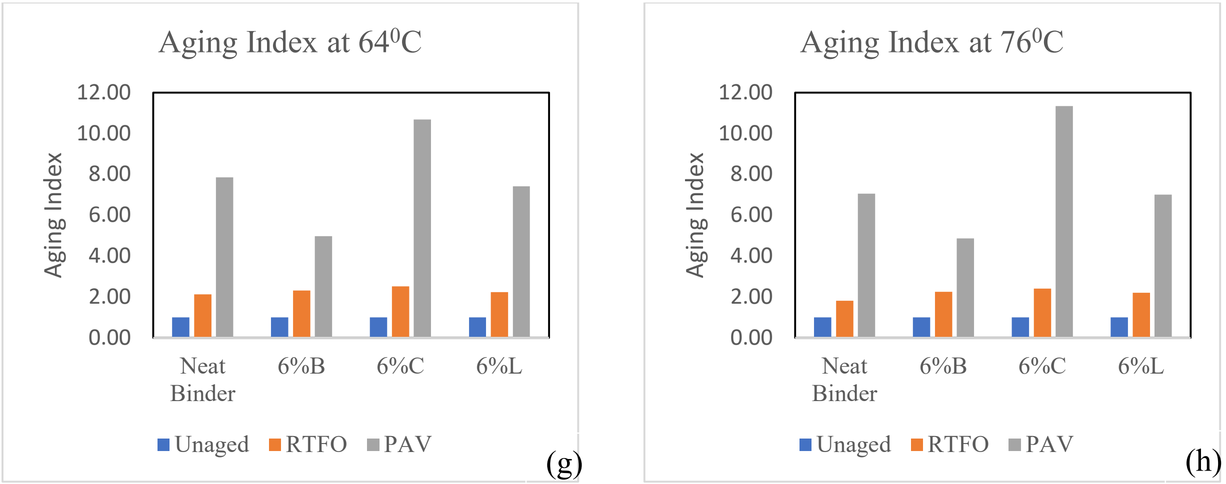


Figure 8: Aging Index data for neat and modified bonders at different temperature

FTIR analysis of aged and unaged samples of lignins, binder, and binder with lignins

Figure 9(a) allows the spectral differences between the three different type of lignins to be seen in the fingerprint region between 1800 and 800 cm^{-1} wavenumbers. All three lignins showed a 865 cm^{-1} vibration associated with guaiacyl lignin [25]. The lignin obtained from black liquor showed a more prominent guaiacyl methoxyl group peak at around 1260 cm^{-1} and a less intense C=O non-conjugated stretching vibration at 1705 cm^{-1} [26]. In the lignin obtained from black liquor, there is no vibration at 1154 cm^{-1}associated with C-O-C asymmetric stretching, found in Cellulose I and II [27]. The vibration at 1365 cm-1 related to C-H deformation from cellulose and hemicellulose is present in all three samples but less intense in “B” lignin [13] Thus, this precipitated "B" lignin may be somewhat purer than the commercial "C" lignin and the rice hull lignin "L."

Figure 9(b) shows the absorbance spectra of base binder partially replaced with varying percentage of “B” lignin from 2 to 6%. As indicated by the concentration, as the lignin concentration in the base binder increased, the intensity of the 1262 cm^{-1} absorption band and other lignin related peaks increased [26]. This shows that the binder was uniformly well-mixed. Similar findings were observed for base binder replaced with either “C” lignin or ‘L” lignin.

Figure 9: FTIR Spectra (a) FTIR Spectra of the three types of lignin in the biomass fingerprint region; (b) FTIR spectra of base binder partially replaced with varying percentage of “B” lignin.

The spectra of all the aged samples, regardless whether or not they included lignin, showed an additional peak at the 1705 cm^{-1} vibration, which is consistent for neat and modified binder with all three types of lignin. This indicates that the vibration at 1705 cm^{-1} absorption band comes from base binder since any type of lignin has no effect. The 1705 cm^{-1} vibration is associated with carbonyl, C=O bonds [28, 29]. In addition, in all samples that included PG-67 binder, with and without lignin, spectral differences were found in the 2000 cm^{-1} to 2200 cm^{-1} region. For the unaged samples, a vibration at 2000 cm^{-1} was more pronounced than that found for the aged samples. This phenomenon suggests that C=C=C allene bonds could be broken during aging, probably by being oxidized to become C=O bonds [30]. At 2200 cm^{-1}, the vibration is again stronger for unaged compared to aged samples. It is thus likely that aging the binder breaks C≡C alkyne bonds in the binder by oxidizing them to C=O [30].

Selection of Suitable Amount and Type of Lignin for HMA

The objective of this study was to improve the binder properties by adding lignin as a modifier. It is desirable to utilize the highest amount of lignin because partial substitution of binder in the mix is also an objective of this study. Among three types of lignin type “C” improves the high temperature grade and reduces the J_{nr} value most. But it has the least strain tolerance and highest AI, making it undesirable for the mix. Type “L” has the highest strain tolerance but does not improve the high temperature grade as much as “B” or “C”. “B” lignin improved the high temperature grade significantly and had a relatively high strain tolerance; most importantly it possesses the lowest value of AI. So, 6% of type “B” lignin was chosen to use for mix preparation for further study.

Mix Test Results

Improved Rut Resistance

Rut depths of 3 control mixes and 3 mixes prepared from lignin B modified binder are plotted in Figure 10. The pair of specimens plotted together are specimens that were tested in same mold and under the same wheel of the tester. The mix prepared with lignin modified binder exhibited 14% less rut depth than the control mix. The modified mix showed lower standard deviation (0.23) than the control mix (0.66 mm) which is an indication of stability under wheel loading and consistency in compaction. Rut depth was measured at two points on each specimen. Considering two values as different data points, a t-test was performed on the average rut depth of the specimens and it was found that there is a significant difference between the average rut depths of the control and modified mixes with 95% level of significance having p-value of 0.009 (< 0.05). So, it can be concluded that lignin modification can successfully improve the rutting resistance of the asphalt mix. As addition of lignin increases the stiffness of the binder, lignin should have the potential of being utilized in Warm Mix Asphalt (WMA) production. The main concern behind the design of WMA is its rutting susceptibility at the initial service life, which is the result of lower binder stiffness attained through reduced short-term aging at the lower production temperature [31].

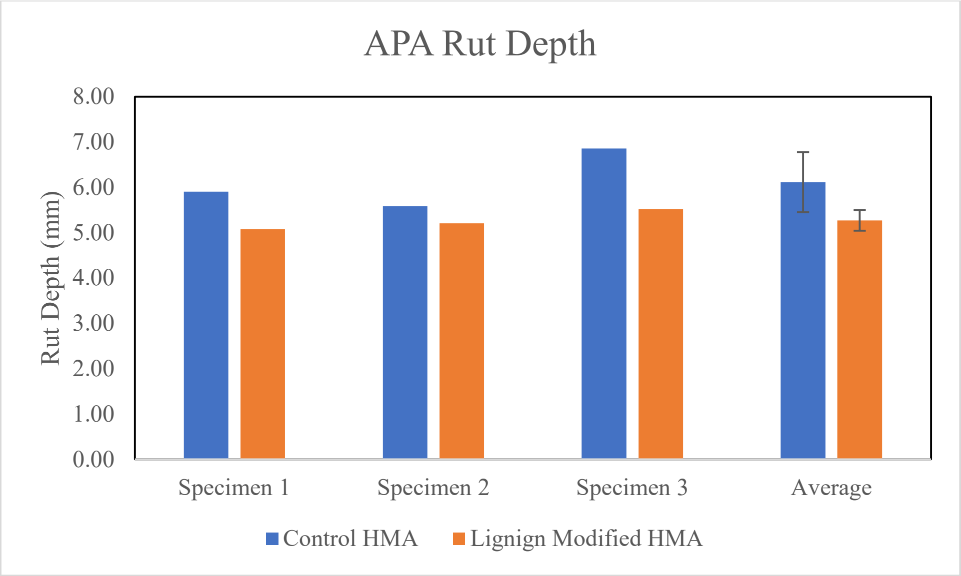
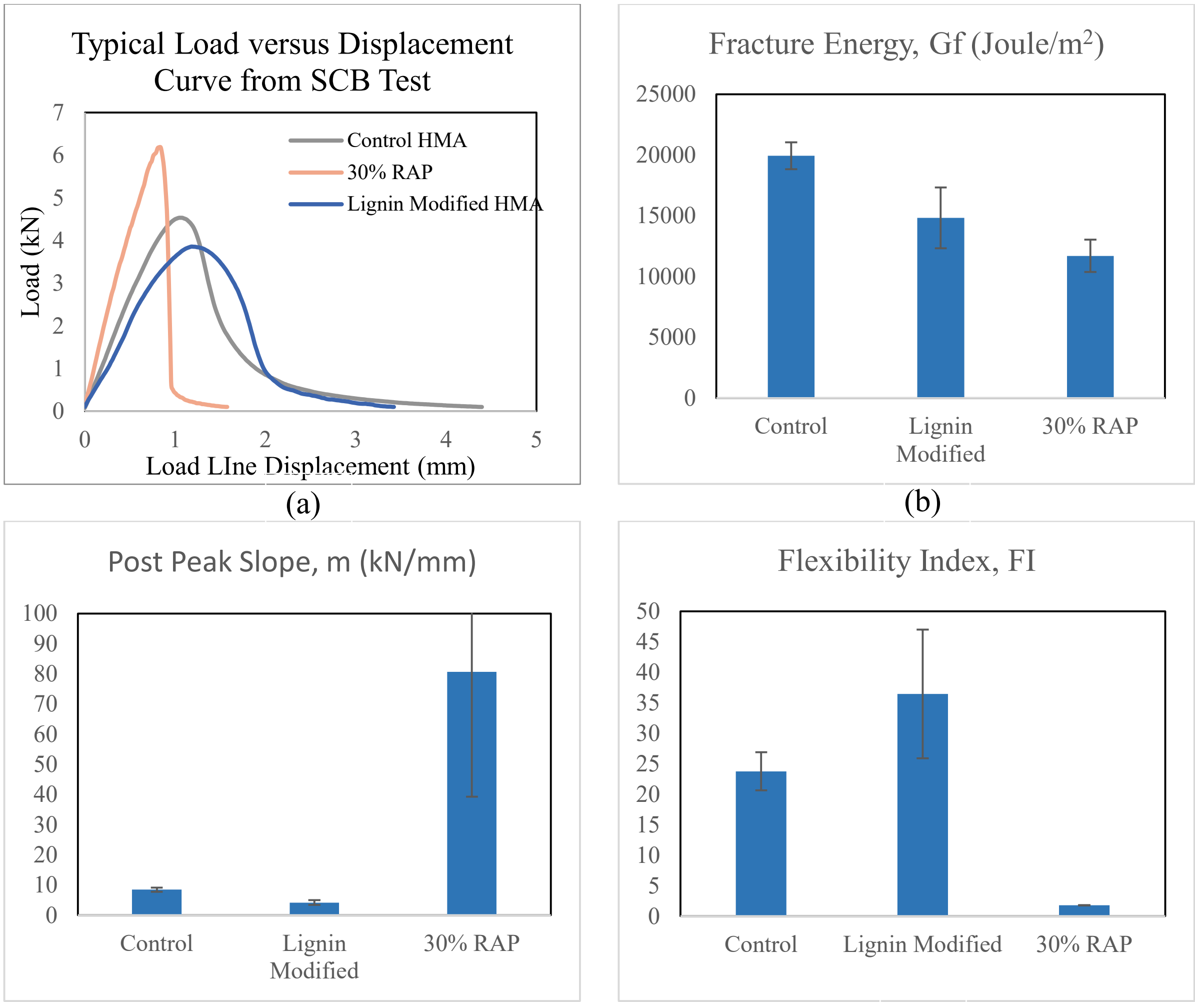


Figure 10: APA rut test result for control and lignin modified mix

Fracture Potential from Semicircular Bent Test (SCB)

A Load-Displacement curve obtained from SCB test along with some test results are plotted in Figure 11. Control HMA and HMA prepared with lignin B modified binder were tested. HMA prepared with 30% reclaimed asphalt pavement (RAP) is included in the plot for better comprehension of the results. In Figure 11(a) typical load-displacement plots are presented for the three above mentioned mixes. Fracture energy is the total area under the load-displacement curve. Lignin modified HMA can withstand a lower load that causes a 25% drop in fracture energy. Though inclusion of 30% RAP can resist higher load it cannot accommodate enough deformation, making it worst among the three mixes with a 40% drop in fracture energy (Figure 11 (b)). It is known that inclusion of RAP makes a mix prone to fracture, but fracture energy itself is not enough to determine the fracture potential of a mix. The fracture energy indicates the overall capacity of asphalt mixture to resist the fracture related damage, but it should not be directly used in structural design and analysis of the pavement [24]. Flexibility Index (FI) determined from SCB test is a measure to identify brittle mixtures that are susceptible to premature cracking. An asphalt mixture can be ranked according to its FI where higher FI implies better cracking resistance. It can be observed that HMA with lignin modified binder has the highest FI, which indicates better cracking resistance than the control HMA at intermediate temperature (Figure 11(d)). FI is proportional to fracture energy and inversely proportional to post peak slope. The higher the value of post peak slope the lower the time it takes to propagate the crack. Among these three mixes unlike HMA, with 30% RAP lignin modified HMA possesses the lowest value of post peak slope (Figure 11(c)) that is an indication of more ductile failure. In case of lignin modified HMA, the post peak slope is 50% lower than control HMA that makes the FI higher even though the fracture energy is lower.



(a)

(b)

(d)

Figure 11: Semicircular bend (SCB) test results

CONCLUSIONS

Replacement of asphalt binder with lignin allows for grade bumping to "E", improves high temperature grade, and enhances percent recovery. However, percent recovery is not as high as can be achieved with polymer-modified binders. Better rut resistance and Flexibility Index is attained in the asphalt mix with lignin replacement, although fracture energy decreases. The aging index decreases after PAV aging with lignin replacement. The moisture sensitivity of the mix is not compromised by 6% of the binder being replaced. Thus, lignin replacement can enhance many properties in asphalt binder and mix.

RECOMMENDATIONS

The positive effects on using renewable, sustainable resources that can be locally-sourced should spur asphalt binder manufacturers to add this to their product. However, further research, including scaling-up of waste biomass extraction of lignin with deep eutectic solvents and more mix tests, leading to field tests, will be required to prove its worth in large scale applications.

ACRONYMS, ABBREVIATIONS, AND SYMBOLS

[Add all the acronyms, abbreviations, and symbols that you used in your report here. For your convenience, a common list has been started for you; please add or delete items to make your list suit your paper and all the terms discussed throughout.]

AASHTO	American Association of State Highway and Transportation Officials
AI	Aging Index
APA	Asphalt Pavement Analyzer
ATR	Attenuated Total Reflectance
cm	centimeter(s)
DES	deep eutectic solvents
DSR	Dynamic Shear Rheometer
FI	Flexibility Index
FTIR	Fourier Transform Infrared
FHWA	Federal Highway Administration
HMA	Hot Mix Asphalt
in.	inch(es)
LADOTD	Louisiana Department of Transportation and Development
LTRC	Louisiana Transportation Research Center
MSCR	multiple stress creep recovery
m	meter(s)
PAV	pressurized aging vessel
RAP	reclaimed asphalt pavement
RTFO	Rolling Thin Film Oven
SCB	Semi Circular Bend
TSR	Tensile Strength Ratio
VFA	Voids filled with asphalt

VMA	Voids in mineral aggregate
WMA	Warm Mix Asphalt

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APPENDIX

N/A