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Replacing Fossil Fuel-Based Asphalt Binder with Lignin Binder from Wastes

SOUTHERN PLAINS
TRANSPORTATION CENTER

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16. Abstract

The goal of this study was to evaluate the effectiveness of using lignin from hydrothermally carbonized rice husks in asphalt materials as a renewable paving material to partially replace a fossil fuel-based binder. The study was conducted in close collaboration between Louisiana Tech University (LTU) Louisiana State University (LSU) and University of Oklahoma (OU). The research team at LTU, extracted lignin from rice husk, prepared modified binders and conducted a series of rheological assessments of the modified binders. The properties and performances of the asphalt mixes prepared with lignin-modified binders were evaluated at LSU and OU. The modification of asphalt binder with lignin exhibited an increase in the rutting resistance in comparison to the neat binder. The low-temperature properties of the asphalt binder were slightly impacted by the addition of lignin. The stability of the binder was found to be significantly enhanced by reducing the lignin particle size along with styrene Butadiene Styrene (SBS) modification. The modification of binder with lignin improved the rutting and moisture-induced damage resistance of asphalt mixes, however, cracking resistance was reduced with lignin addition. The findings indicate that a partial replacement of fossil fuel-based binder with lignin may be feasible but needs further work.

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REPLACING FOSSIL FUEL-BASED ASPHALT BINDER WITH LIGNIN BINDER FROM WASTES

FINAL REPORT
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List of Abbreviations and Acronyms

AC .... Asphalt Content
BBR .... Bending Beam Rheometer
CT_{index} .... Cracking Tolerance Index
DOT .... Department of Transportation
DSR .... Dynamic Shear Rheometer
FHWA .... Federal Highway Administration
HWT .... Hamburg Wheel Tracking
HHV .... Higher Heating Value
HTC .... Hydrothermal Carbonization
IDEAL-CT .... Indirect Tensile Asphalt Cracking Test
IRENA .... International Renewable Energy Agency
JMF .... Job Mix Formula
LaDOTD .... Louisiana Department of Transportation and Development
LSU .... Louisiana State University
LTU .... Louisiana Tech University
MSCR .... Multiple Stress Creep Recovery
NMAS .... Nominal Maximum Aggregate Size
NREL .... National Renewable Energy Laboratory
NTL .... National Transportation Library
ODT .... Oklahoma Department of Transportation
OU .... University of Oklahoma
PG .... Performance Grade
RAP .... Reclaimed Asphalt Pavement
RHDL .... Rice Husk Derived Lignin
RTFO .... Rolling Thin-Film Oven
SBS .... Styrene Butadiene Styrene
TSR .... Tensile Strength Ratio

Executive Summary

With increased focus on renewable energy nationally, availability of fossil fuel-based asphalt binders will become an issue. Consequently, asphalt materials costs are expected to rise significantly. In this context, the pavement industry is looking for viable alternatives to totally or partially replace fossil fuel-based asphalt binder. Utilizing lignin as a partial replacement for binder presents an attractive solution as it is abundant in nature. In this present study, the feasibility of using lignin derived from local agricultural waste, namely rice husks as a partial replacement of asphalt binder was investigated. The effect of the addition of lignin on the properties and performances of asphalt binder and asphalt mixes were explored. The study was conducted in close collaboration between Louisiana Tech University (LTU), Louisiana State University (LSU) and University of Oklahoma (OU). To obtain the objectives of this study, lignin was produced from rice husks using the Hydrothermal Carbonization (HTC) treatment process at LTU. The rice husk derived lignin was then mixed with a PG 67-22 binder using a high shear mixing protocol. The research team at LTU then conducted a series of rheological assessments of the modified binders. The properties and performances of the asphalt mixes prepared with lignin-modified binders were evaluated at LSU and OU. The LSU team selected a commonly available Louisiana asphalt mix and modified with lignin-modified binder. The cracking and moisture-induced damage resistance of the asphalt mix were evaluated by the LSU team. At OU, a commonly used Oklahoma asphalt mix was produced with lignin-modified binders. The rutting and cracking resistance of the asphalt mix were evaluated by the OU team.

It was found that the HTC treatment of rice husks created a powdery substance with an increased acid insoluble lignin content and a reduced cellulose and hemicellulose content. The HTC treatment temperature was found to have significant impact on the production of lignin. The HTC treatment at 250°C was more effective for lignin extraction compared to the treatment at 220°C. In this study, a high shear mixer with a mixing temperature of 170°C was used for preparing lignin-modified binder. The melting point of the lignin was found to be high enough not to melt during the production of lignin-modified binder. Therefore, lignin particles are expected to be present in the modified binders. The storage stability test indicated that the addition of 10% lignin may produce highly unstable modified binder due to the phase separation between lignin and binder. Therefore, continuous stirring of the lignin-modified binder is recommended to reduce phase separation. The stability of the binder was found to be significantly enhanced by reducing the lignin particle size along with polymer modification. The modification of asphalt binder with lignin exhibited an increase in the rutting resistance in comparison to the neat binder. The low-temperature properties of the asphalt binder were found to be negatively impacted by the addition of lignin as it caused an increase in stiffness and reduction in m-value at low temperatures.

Satisfactory moisture-induced damage resistance was observed in asphalt mixes with lignin-modified binders. The Louisiana asphalt mixes prepared with 5% lignin exhibited slightly better moisture-induced damage resistance than that of control mix. Also, the asphalt mixes with lignin-modified binders satisfied the specification requirements for rutting resistance for Oklahoma mixes. An increase in stiffness with the addition of lignin was observed that caused an increase in ITS value. The failure energies of asphalt mix specimens were observed to increase with an increase in lignin content. Also, the post peak slope of the asphalt mix was found to increase significantly with the use of lignin-modified binders. The results indicated that the asphalt mixes became stiff and brittle with the use of lignin-modified binder.

Cracking resistance of the asphalt mixes with lignin-modified binders was found to reduce significantly with the addition of lignin. As the lignin-modified binders did not satisfy the

requirements for fatigue cracking, it was expected that the asphalt mixes with lignin-modified binders will exhibit poor resistance to cracking. The findings indicated that the modification of binder with lignin has potential to improve the properties and performances of asphalt binder and asphalt mix, with the exception of cracking resistance. Therefore, a partial replacement of fossil fuel-based binder with lignin is feasible with measures to improve cracking resistance. In addition, this report includes recommendations on the design, plant production and field construction of asphalt pavement with lignin. Also, a phased plan for future study on this topic is proposed.

Chapter 1. Introduction

1.1 Background

Approximately 94% of the roadway infrastructure within the United States is constructed utilizing asphalt as construction material (NAPA, 2024). Asphalt binders used in the construction of pavements are by-products from crude oil refining process. This process has adverse impact (Thives and Ghisi, 2017; Gaudenzi et al., 2023). With increased focus on renewable energy, availability of fossil fuel-based asphalt binders will become an issue. Consequently, asphalt materials costs are expected to rise significantly. Therefore, the pavement industry is looking for viable alternatives to totally or partially replace fossil fuel-based asphalt binder.

Several renewable alternatives to replace fossil fuel-based asphalt binder have been proposed by different researchers. Many of these alternatives include by-products from various industrial processes, everyday waste, and resources readily available in nature, such as microalgae, swine manure, waste wood or resin, and vegetable oils (Chen et al., 2023; Ji et al., 2017; Escobar-Medina et al., 2021; Wen et al., 2017). These bio-based alternatives offer advantages by reducing landfilling requirements and promoting a circular economy (Peralta et al., 2012). In this context, utilizing lignin as a partial replacement for binder presents an appealing solution.

Lignin is recognized as the second most abundant form of biomass (plant) material present on Earth (Arafat et al., 2019; Gielen et al., 2019). Lignin is produced from various plant species, such as wood bark, pulp, hemp, jute, cotton, flax, and straw. Approximately 50 million tons of lignin are generated annually worldwide as by-products of the pulp and paper industry, with production expected to grow further. However, only a small amount of lignin is currently recovered and being used in material applications (Christopher, 2013). Rice husks represent another abundant and renewable source of lignin. Globally, 150 million tons of rice husk is generated annually that can be used to produce lignin for asphalt applications (Kordi et al., 2024). However, the feasibility of producing lignin from rice husks and the effects of rice husk derived lignin on the performances of asphalt pavement need to be investigated.

The use of lignin in asphalt pavement was first introduced in Europe at the beginning of 1990's (Gaudenzi et al., 2023). However, the topic gained significant interest in the pavement community in the last decade due to the growing demand for renewable solutions. Most research has primarily focused on evaluating the properties of modified binders, while relatively few studies have concentrated on the performances of asphalt mixtures. A number of studies have been conducted to evaluate the compatibility and stability of lignin within asphalt binder (Cai et al., 2022; Xie et al., 2017; Wu et al., 2021). Also, rheological properties, such as high- and low-temperature properties, fatigue cracking, aging and moisture-induced damage resistance of lignin-modified binders were evaluated by several researchers (Nahar et al., 2022; Ghabchi et al., 2022; Yu et a., 2021; Zhang et al., 2020; Zhang et al., 2024). The interaction between asphalt binders and various types of lignin still remains insufficiently understood. Additionally, limited knowledge regarding the effects of lignin on the performance of asphalt mixes has impeded its widespread adoption in pavement construction. Therefore, study is needed to evaluate the effects of lignin derived from local sources on the properties and performances of asphalt binder and asphalt mixes.

1.2 Objectives

In this present study, the feasibility of using lignin derived from local agricultural waste, namely rice husks as a partial replacement of asphalt binder was investigated. The research was conducted in two phases. The first phase focused on the efficient recovery of lignin from local agricultural waste material, while the second phase investigated the properties and performances of lignin on asphalt binder and asphalt mixes. The specific objectives of this study were:

i. To produce lignin from rice husks and prepare modified binders with high amount of lignin;
ii. To evaluate the rheological and chemical properties of the lignin-modified binders;
iii. To evaluate the performances of commonly available Louisiana and Oklahoma asphalt mixes with lignin-modified binders.

1.3 Scope of the Study

This study was conducted in close collaboration between Louisiana Tech University (LTU), Louisiana State University (LSU) and University of Oklahoma (OU). To obtain the objectives of this study, lignin was produced from rice husks using the Hydrothermal Carbonization (HTC) treatment process at LTU. The HTC treatment process was selected for this study due to its lower reaction time, increased lignin production, enhanced energy efficiency, and decreased processing costs (Lynam et al., 2015). The rice husk derived lignin was then mixed with a PG 67-22 binder using a high shear mixing protocol. The research team at LTU then conducted a series of rheological assessments - including high- and low-temperature performance grading, Multiple Stress Creep Recovery (MSCR), and storage stability. The properties and performances of the asphalt mixes prepared with lignin-modified binders were evaluated at LSU and OU. The LSU team selected a commonly available Louisiana asphalt mix and modified with lignin-modified binder. The cracking and moisture-induced damage resistance of the asphalt mix were evaluated by the LSU team. At OU, a commonly used Oklahoma asphalt mix was produced with lignin-modified binders. The rutting and cracking resistance of the asphalt mix was evaluated by the OU team.

Chapter 2. Literature Review

2.1 Use of Bio-Based Alternatives for Asphalt Binders

Bio-based additives or asphalt binder serve as a substitute for petroleum-derived asphalt binder. It is composed of renewable organic elements and can substantially minimize the adverse impact of pavement construction. Waste cooking oil, algae, natural rubber, carbon black, carbon fiber, biochar, cellulose fiber, organic waste e.g., coconut shells, and lignin are some of the bio-based modifiers that have been used with asphalt binder.

Several studies have demonstrated that bio-based additives generated from waste cooking oils had significant promise as asphalt modifiers or regenerators, exhibiting promising performance (Chen et al., 2023). Ji et al. (2017) conducted research on waste cooking oil-based asphalt binder. Waste cooking vegetable oil rejuvenators efficiently restored aging asphalt binders, diminishing hardness and enhancing flexibility at a concentration of 6-8% in comparison to traditional fuel oil-based rejuvenators. The viscosity, Dynamic Shear Rheometer (DSR), and Bending Beam Rheometer (BBR) test results showed that the performance did not deteriorate with the addition of 6% waste cooking oil-based binder compared to the virgin binder. Although rutting resistance of the asphalt binder impacted by the increase in rejuvenator concentrations, the fatigue and low-temperature performance were found to satisfy Superpave design specifications.

Algae is another potential substitute for traditional asphalt binder. Algae grow fast and require no sophisticated cultivation methods; hence could serve as a viable modifier of asphalt binders. Sargassum-modified binder exhibited superior viscosity and rutting resistance compared to the unmodified petroleum-based binder, potentially enhancing high-temperature performance (Escobar-Medina et al., 2021). The primary issue related to sargassum is its lack of chemical affinity with binder. This alteration is due to the physical adsorption of asphalt binder by the sargassum particles, rather than a chemical interaction between the two substances. At concentrations of up to 2.5% by the weight of the binder, it influenced the properties of binder similarly as other powdered modifiers, specifically by enhancing viscosity, elevating the softening point, and improving resistance to permanent deformation (Salazar-Cruz et al., 2021). The sargassum particles were found not to be uniformly dispersed inside the binder at higher concentrations, resulting in agglomeration. Additionally, it was found that the addition of 10% microalgae, by weight of the binder, resulted in notable phase separation (Tabaković, 2020).

Natural rubber and natural rubber latex, being renewable materials, possess the potential to serve as valuable modifiers for asphalt. Prior study indicated that using natural rubber enhances the viscosity and elastic recovery of modified binders, potentially improving asphalt pavements' resilience to rutting, heat cracking, and fatigue damage (Wen et al., 2017). Also, the natural rubber latex diminishes the temperature sensitivity of the modified binders.

In addition, carbon-based materials, including carbon black, carbon fiber, and graphite, exhibited the potential to be used for asphalt modification. The carbon fiber modifier was reported to enhance the rutting resistance of the asphalt binder subjected to high temperatures and alleviate its oxidation process (Yao et al., 2013). Biochar is another organic substance that is high in carbon content. It is primarily generated by pyrolysis of biomass. Prior research indicated that the addition of biochar enhances elastic properties and significantly improves the rutting resistance of the modified asphalt binder (Zhang et al., 2022). The asphalt binder modified with biochar of fine particle size exhibited improved fatigue cracking resistance compared to the asphalt binder modified with coarse particle size biochar. Use of biochar at a mixing ratio of 2% to 4% (by weight of the binder) and a particle size of less than 75 μm was recommended for the modification of asphalt binder.

Cellulose fiber has the potential to be used with asphalt binder to enhance the characteristics of asphalt pavement. Cellulose fiber is an organic fiber derived from the chemical treatment of natural wood (Li et al., 2021). The primary constituents of cellulose fiber include cellulose, hemicellulose, lignin, and other contaminants. A study conducted by Eskandarsefat et al. (2019) assessed the influence of four varieties of cellulose-based composite fibers on the characteristics of neat and polymer-modified binders. Cellulose fibers significantly improved the penetration, softening point, and viscosity of the neat and polymer-modified binders. The use of cellulose-glass fibers exhibited the most substantial enhancements, minimizing the drain down and permanent deformation. Rubberized fibers reduced viscosity and softening point while improving penetration. The three-dimensional network created by the fibers within the asphalt binder was found to be responsible for improving binder characteristics. However, the efficacy of fibers is contingent upon the composition, dosage, and source of the fibers. Nanomaterials obtained from organic waste, such as coconut shells, provide an eco-friendly alternative to reducing waste and improving construction materials. Coconut shells, owing to their durability and quality, are especially advantageous for the production of nanomaterials, such as Nano-Charcoal Ash (NCA). According to a recent study done by Jeffry et al. (2018), binder treated with NCA exhibited enhanced physical and rheological characteristics. The extensive surface area of NCA improved binder cohesiveness and rigidity, hence improving resistance to rutting and fatigue cracking.

Lignin is one of the most abundant biopolymers which has great potential to replace fossil fuel-based asphalt binders. Lignin is produced from industrial and agricultural byproducts. It is a polymeric molecule characterized by a network of spatial structures and a chemical composition rich in highly reactive phenolic and alcoholic hydroxyl groups (Peng et al., 2020). Despite lignin being the one of the most prevalent biopolymers on earth, minimal quantities have been converted into value-added bioproducts. Annually, around 50 million tons of lignin are produced by the pulp and paper industry, although hardly 2% of this waste lignin has been repurposed for bioproducts (Xie et al., 2017). The variability and complexity of lignin complicate the prediction of its impact on the thermal properties of asphalt binder at both high and low temperatures. Arafat et al. (2019) reported that substituting fossil fuel-based binder with lignin can enhance rutting resistance while keeping the resistance to moisture-induced damage unchanged. Also, improved cracking resistance was observed for the asphalt mixes with lignin-modified binders, as demonstrated by Louisiana Semi-Circular Bend (SCB) test. However, the effect of a higher lignin content on the properties of asphalt binder and asphalt mix has not yet been explored. The purpose of this research is to examine a higher lignin concentration (up to 10%) and analyze the physical and chemical properties of lignin-modified asphalt binder and asphalt mix.

2.2 Production of Lignin from Biomass

Typically, lignocellulose biomass is broken down into cellulose, hemicellulose, and lignin to extract lignin (Abdelaziz et al., 2016) The processes generally involve three major steps, namely pretreatment, extraction, and purification (Tarasov et al., 2018). Each of these processes involved a series of steps for the production of lignin.

Pretreatment of the biomass source plays a significant role in the final product's yield and quality (Chen et al., 2017). Pretreatment processes are typically classified by four different types, namely physical, physicochemical, chemical, and biological (Tanis et al., 2024).

Mechanical treatments, microwave treatment and high-energy electron radiation are examples of the physical pretreatment processes (Chen et al., 2017). These methods are simple but energy intensive. In chemical pretreatment process, solvents and reagents, such as acids, alkalis, organic alcohols and ionic liquid are used to break down the lignin, cellulose, and hemicellulose system by solubilization of the lignin components. Chemical pretreatment processes have better selectivity, efficient processing timeframes, and high-quality bioproduct recovery over physical pretreatment processes. Disadvantages of the chemical pretreatment process are toxicity, corrosive reagents, as well as high capital investment cost (Chen et al., 2017; Hassan et al., 2018). The physicochemical methodologies integrate both physical and chemical processes for the treatment of lignocellulosic biomass. Steam explosion, ammonia fiber expansion, supercritical fluids, and wet oxidation (Li et al., 2022) are some examples of physiochemical processes that present unique advantages in comparison to solely physical or chemical pretreatment techniques for the extraction of lignin. In the biological pretreatment process, microorganisms such as fungi, bacteria, or their enzymes (Abdelaziz et al., 2016; Li et al., 2022) are used to selectively extract the lignin, not compromising cellulose and hemicellulose quality. One of the major advantages of biological pretreatment is no usage of toxic chemicals. However, pretreatment time is longer because of the slow hydrolysis rate which is a major drawback of this process (Hassan et al., 2018; Li et al., 2022).

Depending on the requirements of the final product, the extraction process differs in chemicals used, process parameters, and process conditions. Many researchers have already applied different extraction methods, such as organosolv treatment (Ramakoti et al., 2019; Ligero et al., 2008), hydrothermal treatment (Lourencon et al., 2020), hydrolysis (acid and alkali) (Khazraie et al., 2017), acid treatment (Zhang et al., 2010), deep eutectic solvents (Lou et al., 2019), and ionic liquids (Pu et al., 2007) to produce lignin. Lignin produced by different processes varies in lignin yield percentage, purity, and types of the final product.

Different processes, such as centrifugation (Tarasov et al., 2018), membrane-based separation (Servaes et al., 2017), filtration, ultrafiltration, solvent-based precipitation, acid-alkali treatment, etc. are used in the purification process of lignin. In a study by Dagnino et al. (2018), rice husk was treated with 8% NaOH and ethanol/water (54:46, v/v) at 152℃ for 100 minutes. By varying the process time and temperature, a maximum lignin removal of 91.7% was obtained by the researchers. In another study, formic acid was used as an organosolv solvent (88%) at 60℃ for a duration of 8 hours on corn as a biomass source. The removal efficiency was observed as 70% (Zhang et al., 2010). Several other researchers used banana rachis, bamboo chips, and rice straw as biomass sources and treated them with formic acid, NaOH, and ammonia (in dilute acid) with different concentrations and process parameters with yields ranged between 45% and 96% (Kumar et al., 2018; Florian et al., 2019; Kim et al., 2011).

Hydrothermal carbonization (HTC) is a thermochemical process that turns biomass into a solid, coal-like product with a higher calorific value and more carbon, called hydrochar. Previous studies have reported that in comparison to biomass feedstock, hydrochar exhibits a superior Heating Value (HHV) and elevated carbon content (Lynam et al., 2015). Dinjus et al. (2011) investigated the impact on the lignin component of biomass with HTC treatment. It was reported that the HTC treatment only transformed the soluble components of the biomass while the original structure of the lignin was mostly preserved (Dinjus et al., 2011). This finding likely results from the complex composition of lignin. Lignin units are interconnected through several ether and carbon-carbon linkages, with the β-O-4 ether bond being the predominant connection in plant materials. The β-O-4 linkage constitutes roughly 48−60% of the total interunit connections in native type lignin (Małachowska et al., 2021; Wikberg et al., 2015). Thus, HTC treatment appears to be a viable way to separate lignin from other components found in biomass. In a recent study, hydrochar derived from corn stalks was added to asphalt binder using the wet method (Wu et al., 2021). The interaction between the hydrochar and binder factions was identified by chemical analysis, leading to low compatibility but satisfactory anti-aging properties. In another study, Walters et al. (2014) found that the inclusion of hydrochar, obtained through a filtration process following the production of bio-binder, might enhance the rheological properties and aging resistance of asphalt (Walters et al., 2014). Several research concluded that the miscibility of asphalt binder and biomass-derived lignin will depend on particle size, amount of biomass added, and the reaction temperature during hydrothermal carbonization process (Zhang et al., 2018; Yang et al., 2017). However, Yaro et al. (2023) mentioned that no chemical reaction occurs throughout the asphalt binder modification procedure, indicating that the incorporation of lignin in the asphalt binder is predominantly attributed to its physical features rather than its chemical characteristics (Yaro et al., 2023).

2.3 Effect of Lignin on the Properties of Asphalt Binder

A number of studies were found to evaluate the effects of the incorporation of lignin in asphalt binder. Table 1 shows the advantages and disadvantages of using lignin as a modifier of asphalt binder as observed by other researchers. Several studies showed that lignin modification enhanced asphalt binder's resistance to rutting and fatigue cracking while simultaneously improving performance through diminishing dependence on fossil fuel (Nahar et al., 2022; Ghabchi et al., 2022; Zhang et al., 2020; Zhang et al., 2024). Nahar et al. (2022) evaluated the effect of partial replacement of asphalt binder with unmodified and chemically modified lignin. The compatibility and rheological properties of the lignin-modified binders were assessed. It was found that the addition of lignin caused stiffening of the binder. The extent of the change in binder properties depended on the extent and type of modification. The modified binder showed an improvement in the high-temperature properties and introduced more flexibility to the low-temperature properties. Ghabchi et al. (2022) evaluated the effect of three different lignin types on the rheological properties of the asphalt binder, aging characteristics, and its adhesion to different aggregates. The study reported that different lignin types have significantly different effects on the rheological, aging, and adhesion properties of the binder. However, incorporating lignin in the PG 58-28 asphalt binder improved resistance to rutting. Wu et al. (2021) conducted a series of tests, including empirical, viscosity, rutting, fatigue, cracking, stability, and chemical tests to determine the influence of soda lignin on asphalt binder. The rheological performance test results revealed that the addition of soda lignin significantly enhanced the rutting resistance and fatigue performance of asphalt binder. A study conducted by Xu et el. (2017) found that the addition of 5% lignin caused considerable reduction of fatigue life. In a recent study conducted by Zhang et al. (2024) demonstrated that lignin significantly improves the resistance to moisture-induced damage of asphalt materials. This improvement is related to the modifications in the surface morphology and adhesive characteristics of the asphalt binder upon its modification with lignin (Zhang et al., 2024). The aging performance of lignin-modified binders was investigated by Batista et al. (2018). The results indicated that the incorporation of lignin could enhance the aging resistance of asphalt binders due to the low carbonyl index (Batista et al., 2018).

A number of studies reported that the low-temperature properties of asphalt binder could be negatively affected with the addition of lignin. Xu et el. (2017) performed Bending Beam Rheometer (BBR) test and found that the addition of wood-derived lignin to binder slightly worsened the low-temperature properties of the binder. Xie et al. (2017) reported that the addition of water-insoluble lignin had insignificant effects on the low-temperature performance when added at 5%−10% by the weight of the binder. However, the addition of 20% lignin significantly reduced the low-temperature performance of asphalt binder.

Storage stability is widely viewed as the major hindrance to the promotion of lignin-modified binders. According to several studies, the compatibility of lignin and asphalt binder might be challenging and can result in phase separation and lower effectiveness (Cai et al., 2022; Xie et al., 2017). This phenomenon is especially pronounced in instances where lignin remains chemically unchanged or when the molecular interactions are inadequately optimized (Cai et al., 2022; Xie et al., 2017). Wu et al. (2021) performed a segregation treatment on the lignin-modified binders and found that the lignin concentration was significantly different between top and bottom parts. The study suggested remixing the lignin-modified binders to achieve homogenous concentration before adding into asphalt mixes. Pérez et al. (2019) reported that the addition of 40% lignin, derived during the production of hardboard panels, resulted in a modified binder that is not suitable for storage. A study conducted by Yu et al. (2021) investigated the storage stability of asphalt binder modified by soda lignin powder. The dispersion of soda lignin powder in asphalt binder was found to be uniform and stable, indicating good compatibility between lignin powder and base asphalt. Therefore, the rheological properties of the lignin-modified binder will depend on the origin and properties of lignin biomass.

Table 1. Advantages and disadvantages of using lignin in asphalt binder

Asphalt Binder	Lignin	Lignin %	Mixing Procedure	Rheological Property Improved	Rheological Property Degraded	Ref.
Pen-60/70	Soda	5%,10%, 15%,20%, Opt. 15%	4000rpm, 8000rpm, 155°C, 50min	Rutting & Fatigue Resistance	Cracking Resistance	Yu et al. (2021)
Pen-70	Wood Lignin (Paper Industry)	Lignin: Binder (1:4 by mass)	High Shear Mixer	Softening Point, Complex Modulus, Anti-Aging (Long Term)	Penetration, Ductility, Anti-aging (Short Term)	Wu et al. (2021)
PG64-22, PG76-22	Wood Lignin (Sigma Aldrich)	5%, 10%	1500rpm, Regular Shear Mixer, 30min, 163°C	Rutting Resistance, Viscosity, Anti-Aging (Long & Short Term)	Cracking & Fatigue Resistance,	Xu et al. (2017)
Pen-70	Wood Lignin & Lignin Fiber	10%	High Shear Mixer 3000 rpm, 30 min, 163°C,	Moisture Stability, Fatigue, Rutting & Cracking Resistance		Zhang et al. (2020)
Pen-60/70	Lignin (Black Liquor)	3%, 6%, 9%, 12%. Opt. 6%	5000 rpm, 30 min, High Shear Mixer	Permeability Index, Viscosity	Marshall Stability (Lignin>6%)	Zahedi et al. (2020)
Pen-40/50	Soda Lignin (Pinus Wood Sawdust)	2%, 4%, 6%	3000 rpm, 30 min, 160°C	Softening Point, Penetration Index, Viscosity.	Ductility	Asad and Albayati (2024)

2.4 Effect of Lignin on the Performance of Asphalt Mixes

Most of the previous literature was found to focus on the characterization of asphalt binder modified with lignin. The effects of the addition of lignin on asphalt mixes were demonstrated in a few previous research studies. Arafat et al. (2019) evaluated the rutting, cracking, and moisture-induced damage susceptibility of an asphalt mix prepared with 6% lignin-modified asphalt binder. In this study, lignin was precipitated from black liquor. Improved rutting resistance was observed from the lignin-modified asphalt mix, without sacrificing moisture-induced damage resistance. Better cracking resistance with respect to increased flexibility index was observed from the Semi-Circular Bend (SCB) test. Zahedi et al. (2020) examined the effect of lignin on Marshall stability, resilient modulus, and fatigue life of asphalt mixes. The presence of lignin increased stability, reduced flow and expected to improve rutting resistance. The fatigue life of asphalt mix was found to be positively affected by adding 3 to 6% of lignin to the asphalt mix. Increasing the amount of lignin reduced the fatigue life of asphalt mix. Pérez et al. (2019) conducted the repeated load axial test to evaluate the resistance to permanent deformation. The asphalt mixes made with 20% of industrial waste presented lower permanent deformation than the control mix. However, after 6 months of curing time, the differences between the control and modified mixes were not noticeable. Moreover, experimental results from the Rolling Bottle test confirmed that the presence of lignin enhances affinity between binder and aggregate. Fatemi et al. (2022) evaluated the durability of asphalt mixes containing Calcium Lignosulfonate (CLS) powder as a binder modifier. The results indicated that the asphalt mixes became stiff due to the combination of CLS and binder, which significantly improved the rutting resistance of asphalt mixes. Gaudenzi et al. (2022) evaluated the effect of two different lignins on the binder-aggregate adhesion, Indirect Tensile Strength (ITS), stiffness modulus, thermal susceptibility, fatigue resistance, and low-temperature cracking of mixes. The presence of lignin did not compromise the bond strength between bio-binder and aggregate. The ITS value of the asphalt mixes with lignin were found to be higher than the control mix. However, the fatigue cracking resistance was reduced with the addition of lignin.

Chapter 3. Materials and Methodologies

3.1 Preparation of Lignin for Binder Modification

3.1.1 Collection of Rice Husks
The lignin required for this study was extracted from rice husks. For this purpose, rice husks were collected from Falcon Rice Mill located at Crowley, Louisiana. The raw rice husks were dried for 24 hours in an oven at 105°C to remove moisture. The dried rice husks were then stored in a closed plastic bag in a refrigerator (~4°C) until use. The diameters of the rice husk particles were between 850 and 1405 microns, as they were sieved through No. 14 and No. 20 sieves with the middle portion selected for HTC treatment.

3.1.2 Hydrothermal Carbonization (HTC) Treatment
In this study, the HTC treatment on the rice husks was performed using a 2 Liters Parr reactor (4848 bench-top reactor, Parr Instrument Company, Moline, Illinois) available at Louisiana Tech University. The steps involved in the HTC treatment process are shown in Figure 1. For this purpose, 75 grams of dried rice husk sample was mixed with 750 grams of deionized water (solvent) in a glass liner. The temperatures used for the HTC treatment were 220°C and 250°C. Once the reactor reached the set temperature, the reaction continued for 10 minutes. The reactor vessel was then lowered into a cold-water bath to quench the reaction. The pressure and temperature were recorded every 10 minutes. The final products consisted of solid hydrochar that is high in lignin and a sugar solution.

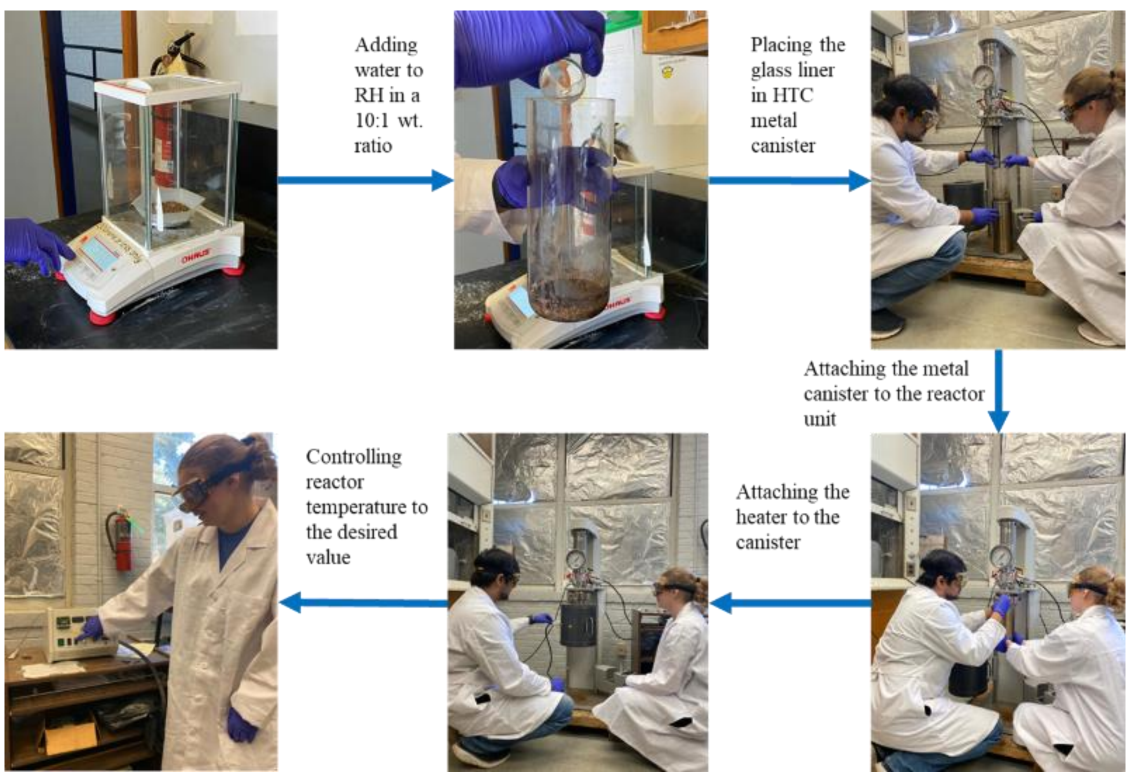


Figure 1. Steps involved in lignin production from rice husk using HTC treatment process

Once cooled, the biomass was separated from the solvent using nylon membrane filters (pore size 0.45 µm, diameter 90 mm) and a mesh filter membrane. A filtration unit was set up by connecting a Buchner funnel with a filter and a filtration flask to a vacuum pump. The filtered biomass was dried at 105°C for 24 hours prior to weighing, to ensure all moisture was removed. In this study, we refer to this filtered, dry hydrochar as Rice Husk Derived Lignin (RHDL).

3.1.3 Characterization of Lignin

Determination of Lignin Content of Rice Husk

The lignin content before and after the HTC treatment was quantified following the protocols outlined by the National Renewable Energy Laboratory (NREL) using procedure NREL/TP-510-42618 (Sluiter et al., 2012). Figure 2 shows the steps involved in this analysis.

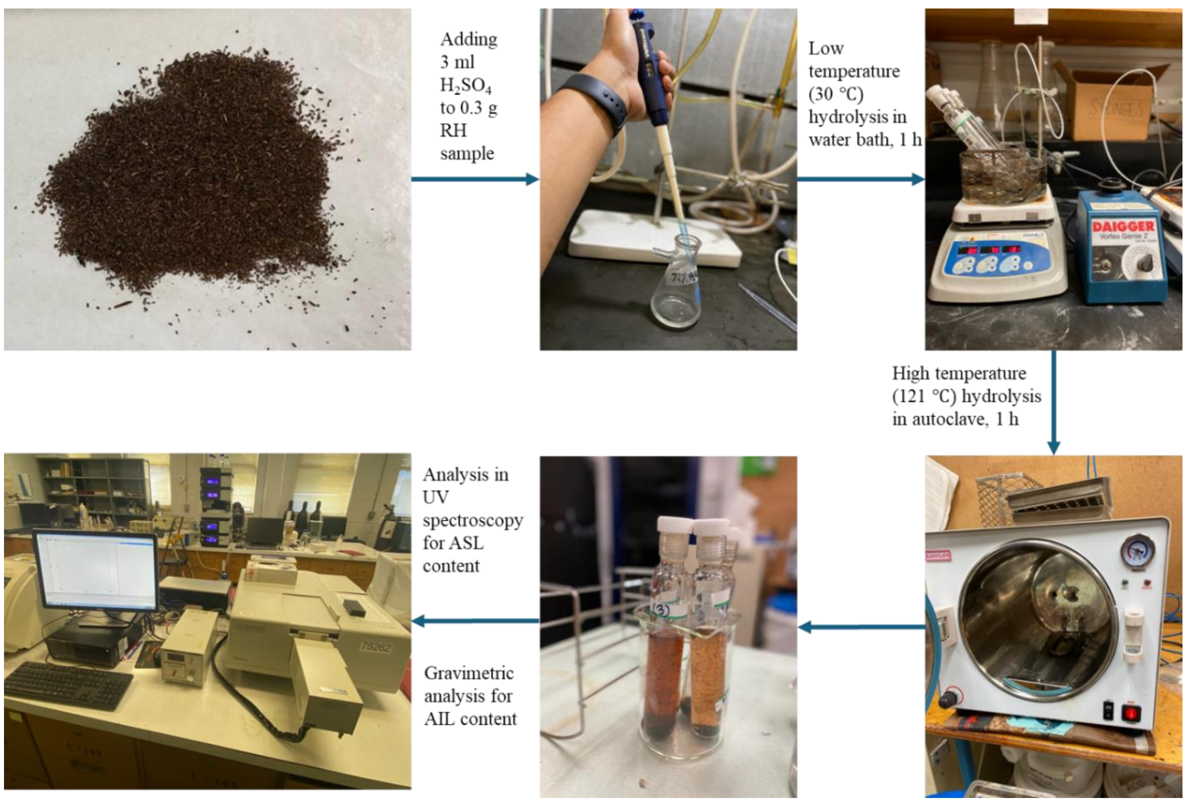


Figure 2. Experimental steps for analyzing lignin content in rice husk using NREL protocol

The mass yield of lignin, Acid Insoluble Lignin (%AIL), Acid Soluble Lignin (%ASL) were calculated using Equations 1, 4 and 5, respectively. Equations 2 and 3 were used to calculate %AIR and %Ash to determine the %AIL and %ASL. The hydrochar used in these equations represents the rice husk after HTC treatment. The details of the calculation can be found in Islam et al. (2024). The wavelength used for the absorbance calculation in Ultra-Violet (UV) spectroscopy for the ASL calculation was around 280 nm. The uniformity of wavelength was seen in almost all samples of rice husk. The path length was 1 cm, the amount of filtrate was 86.73 ml, and the absorptivity (ε) was 12 L/g cm.

$$mass\ yield = \frac{mass_{hydrochar}}{mass_{untreated\ rice\ husk}} \times 100\%$$

Equation 1

$$\%AIR = \frac{(Cruicible\ wt.+Residue\ wt.)-Crucible\ wt.}{Oven\ dry\ wt.of\ sample} \times 100\%$$

Equation 2

$$\%Ash = \frac{(Cruicible\ wt.+Ash\ wt.)-Crucible\ wt.}{Oven\ dry\ wt.of\ sample} \times 100\%$$

Equation 3

$$\%AIL = \%AIR - \%Ash$$

Equation 4

$$\%ASL = \frac{UV_{abs} \times Volume_{filtrate} \times Dilution}{\varepsilon \times Oven\ dry\ wt.of\ sample \times Pathlength} \times 100\%$$

Equation 5

Higher Heating Value (HHV) of Combustion

The Higher Heating Values (HHV) of combustion for lignin were determined using an adiabatic oxygen bomb calorimeter (1341EB bomb calorimeter; Parr Instrument Company) equipped with continuous temperature monitoring. Samples were subjected to a drying oven at 105°C for 24 hours before analysis. A sample of approximately 0.5 gram was measured into a metal crucible, and 10 cm of fuse wire was shaped to contact the upper portion of the biomass. The sample was then oxygenated to a pressure of 3.04 MPa within the vessel. One liter of DI water was then introduced into the calorimeter. The beginning water temperature, initial crucible mass, initial fuse wire mass, biomass sample mass, final water temperature, crucible mass post-ignition, fuse wire mass post-ignition, and ash mass were recorded. Three replicates were tested to determine the standard error of HHV of lignin.

Fourier Transformed Infrared (FTIR) Spectrometer

The rice husk and rice husk derived lignin samples were analyzed using a ThermoScientific Nicolet 6700 Fourier Transformed Infrared (FTIR) spectrometer. The spectrometer collected spectra by performing 32 scans with a resolution of 4 cm^{-1}. The FTIR examined wavenumber ranged from 4,000 to 400 cm^{-1}. The spectrum of a pure Potassium Bromide (KBr) pellet was initially acquired and established as the background for all subsequent samples. The rice husk and lignin samples were milled using a planetary ball mill (Across international, Livingston, New Jersey; Model: PQ-N4) prior to the FTIR analysis. Approximately 0.001 grams of sample were combined with 0.100 grams of KBr to make each KBr pellet. Three distinct pellets were examined for each sample. The spectra obtained were analyzed with OMNIC software (version 8.2.0.387) using the area method.

3.2 Modification of Binder with Lignin

The work-flow diagram for the production and characterization of lignin-modified binders is presented in Figure 3. In this study, a PG 67-22 binder was used as a base binder and the lignin obtained from HTC treatment was used as a modifier. Figure 4 shows the process involved in binder modification with lignin. At first, a quart can of binder was heated at 170°C in a forced draft oven for approximately 2 hours. The apparatus was then placed within a heating mantle to ensure uniform temperature throughout the can. A thermometer was utilized to measure the temperature at 3 to 4-minute intervals to maintain the temperature within the range of 160°C to

170°C. A high shear mixer was then introduced inside the can to stir the base asphalt binder. The rotational velocity (Rotation Per Minute (RPM)) of the high shear mixer was increased carefully. The required amounts of lignin (5% and 10% by weight of the binder) were then gradually added into the asphalt binder. To enhance the rate of dispersion while preventing agglomeration at the top, a spatula was dipped into the quart can and mixed by hand. During the initial 30 minutes, the rotational velocity was maintained at 4000 RPM. For the subsequent 20 minutes, it was increased to 8000 RPM. After 50 min of blending at a temperature between 160°C and 170°C, the lignin appeared to be thoroughly blended within the asphalt binder. Upon the completion of the mixing process, the quart can was carefully removed and placed in a secure location.

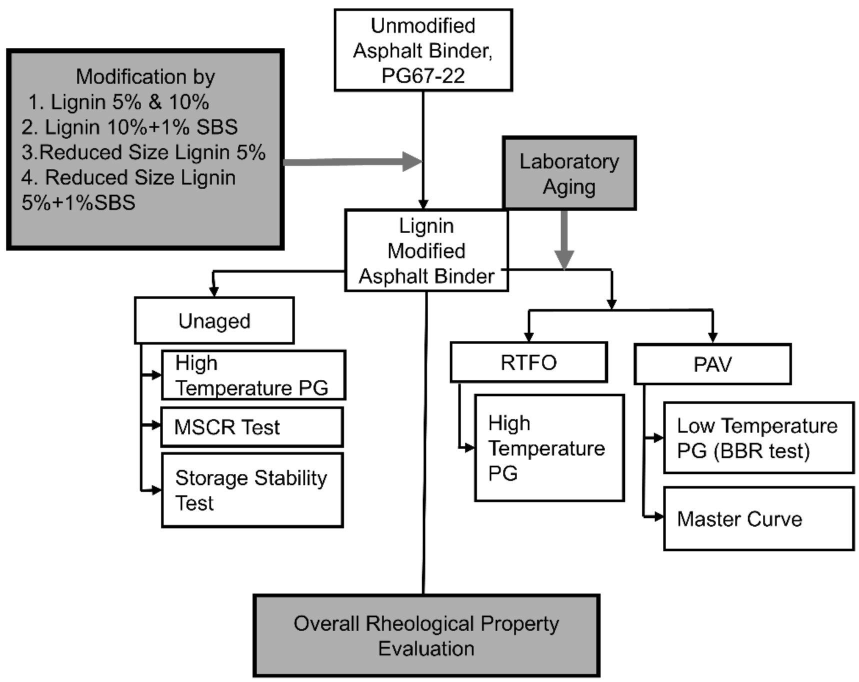


Figure 3. Workflow diagram for characterization of lignin-modified binder

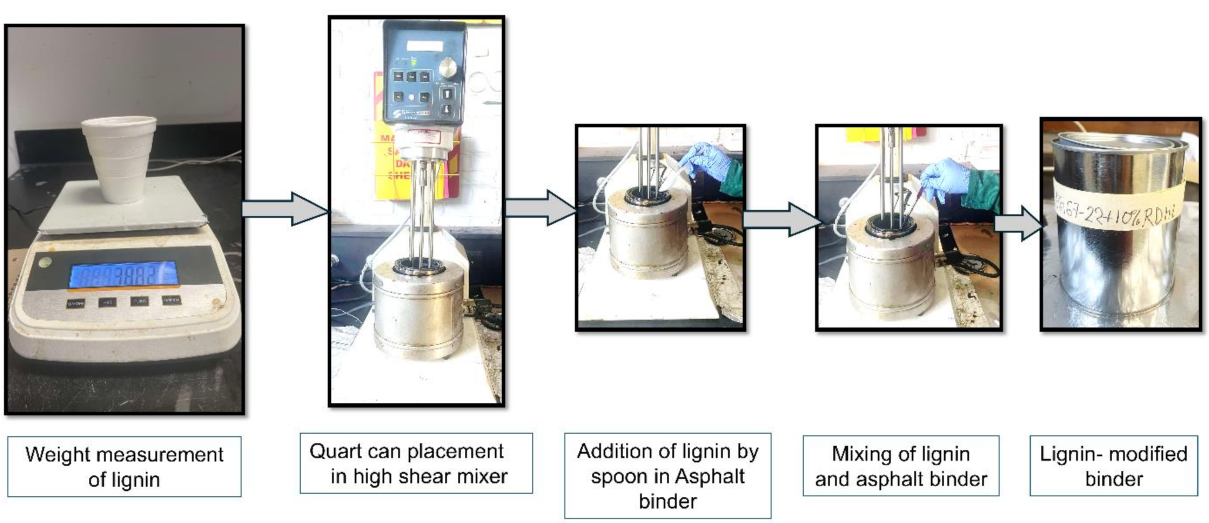


Figure 4. Steps of binder modification with lignin

3.3 Production of Modified Binders with Lignin of Different Particle Sizes

To evaluate the effect of particle size on the stability of the modified binder, the particle size of the obtained lignin was reduced using the following procedure. Initially, the lignin was preserved in an air-cooled refrigerator, at temperatures around 4°C for a duration of two hours using a zip-lock plastic bag. Immediately after taking out the sample from the refrigerator, the lignin was crushed using a hammer. At the time of hammering, another zip-lock bag was used to ensure no tearing of plastic bag and loss of lignin. This procedure was executed manually and required approximately 10 to 15 minutes. Upon the conclusion of the size reduction process, the lignin particles were subjected to sieving through a No. 80 (180 μm) sieve. All particles passed through the No. 80 sieve. A similar sieving procedure was conducted utilizing a No. 200 (75 μm) sieve. However, only a minimal quantity of particles was able to pass through No. 200 (75 μm) sieve. Therefore, it was assumed that the dimensions of the reduced lignin particles were within the range of 75 μm to 180 μm (passing no. 80 sieve and retaining on #200 sieve).

The particle size distributions of the lignin were observed under a Laser Scanning Confocal Microscope (LSCM). Figures 5(a) and 5(b) show the photographic views of the lignin before and after size reduction, respectively. Figures 5(c) and 5(d) show images of the lignin before and after size reduction obtained using the LSCM. The LSCM images indicate that without size reduction, lignin particles are flat and elongated. The reduced particles of the lignin were mixed with asphalt binder following the same procedure followed before. Also, in this study, the effect of using Styrene-Butadiene- Styrene (SBS) polymer on stabilizing lignin modified binder was investigated. For this purpose, 1% SBS polymer, by weight of the binder, was added to the 10% lignin- and 5% reduced size lignin-modified binders using the previously mentioned procedure.

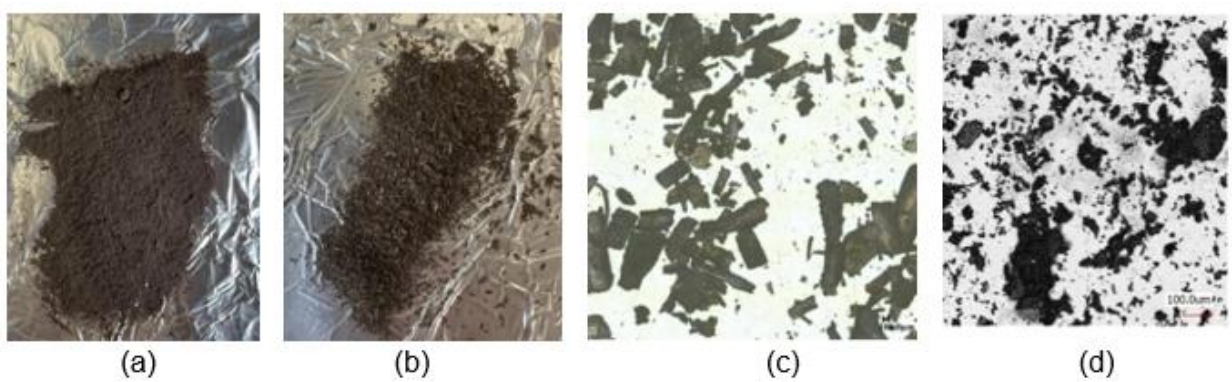
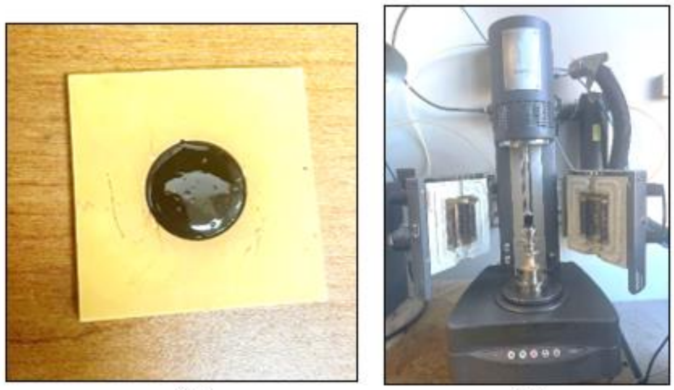


Figure 5. lignin particles (a) before particle size reduction; (b) after particle size reduction; (c) LSCM image before size reduction; (d) LSCM image after size reduction

3.4 Characterization of Lignin-Modified Binders

3.4.1 High- and Low-Temperature Performance Grades (PG)

The Dynamic Shear Rheometer (DSR) tests were conducted on unaged and short-term aged binders to determine their Superpave PG grade, complex modulus (G*) and phase angle (δ) in accordance with the AASHTO T 315 (AASHTO, 2022) test method (Figure 6). The short-term aging of the binders were conducted using a Rolling Thin Film Oven (RTFO) in accordance with the AASHTO T 240 (AASHTO, 2018) method. The binder samples were prepared using a 19 mm silicon rubber mold. A sample diameter of 25 mm and thickness of 1 mm were used for DSR testing at high temperatures. The rheological properties (G* and δ) from the test were used to determine the rutting factor (G*/ sin δ) and the high-temperature PG grade. At OU, the intermediate temperature properties of the 0% and 10% lignin-modified binders were evaluated using the fatigue parameter (G*. sin δ). For this purpose, modified binders were long-term aged using a Pressure Aging Vessel (PAV). The DSR test was then conducted on the PAV-aged asphalt binder samples of a diameter of 8 mm and thickness of 2 mm at intermediate temperatures.



(a) (b)

Figure 6. Dynamic Shear Rheometer (DSR) test: (a) binder sample and (b) test device

The Bending Beam Rheometer (BBR) tests (Figure 7) were conducted only on long-term aged binders to determine their low-temperature properties. A Pressure Aging Vessel (PAV) was used for simulating long-term aging of the binder in accordance with the AASHTO R 28 (AASHTO, 2022) method. The flexural creep stiffness (S) and rate of stress relaxation (m-value) of the binder samples at low temperatures were determined as per the AASHTO T 313 (AASHTO, 2012) method. In this method, simply supported asphalt beam samples (length = 127 mm, width = 12.7 mm, and thickness = 6.35 mm) were subjected to a constant load (980 ± 50 mN) applied at the mid-point at low temperatures. The test beam was placed in a fluid bath under controlled temperature and loaded for 240 seconds. The S and m-values at 60 seconds were used to quantify thermal cracking resistance of the blended binders. Also, the low-temperature grade of blended binders was determined using the BBR results.

(a) (b)

Figure 7. Bending Beam Rheometer (BBR) test: (a) sample preparation and (b) test device

3.4.2 Multiple Stress Creep Recovery (MSCR) Test

To understand the elastic property of the lignin modified binders, the %Recovery and the non-recoverable creep compliance (J_{nr}) of the modified binders were assessed through the Multiple

Stress Creep Recovery (MSCR) Test. The AASHTO T 350 (AASHTO, 2022) test method was followed to conduct the MSCR test. The sample preparation same as the DSR test was used for this purpose. The test was conducted at 64°C temperature at two stress levels, namely, 0.1 kPa and 3.2 kPa. Each stress level consists of twenty loading-unloading cycles. Each cycle consists of a one-second creep loading and a nine-second recovery period. The non-recoverable creep compliance (J_{nr}) and the %Recovery were calculated from the MSCR test results. The non-recoverable creep compliance was calculated by dividing the non-recoverable strain after each creep and recovery cycle with the corresponding applied stress.

3.4.3 Rheological Master Curve

In this study, the frequency sweep test was conducted using DSR equipment to develop complex modulus, phase angle, storage modulus and loss modulus master curves of the lignin-modified binders. The test was conducted at 70˚C, 52˚C, 25˚C, 0˚C and 10˚C with angular frequency varied between 0.1 to 100 rad/s. A reference temperature of 25˚C was chosen to generate the master curves.

3.4.4 Storage Stability Test

The storage stability test following the ASTM D7173 (ASTM, 2022) test method was used to evaluate the stability of the lignin-modified binders. The storage stability test is widely employed to simulate the degree of separation between polymer and asphalt binder in a laboratory setting. After preparation, the modified binders were poured into aluminum tubes of diameter of 1 inch and height of 5.5 inch (Figure 8). The tubes were then placed vertically, sealing the opening. The tubes were placed inside an oven at 163°C for 48 hours. Then, the tubes were transferred to a freezer for 4 hours for cooling. Finally, the tubes were taken out and cut into three equal parts. The binders from the top and bottom segments were extracted and the high-temperature rheological properties from DSR test were compared to evaluating the stability of the lignin-modified binders during storage.

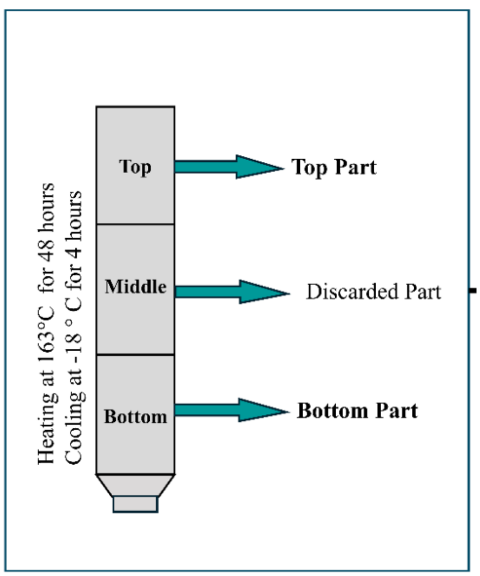


Figure 8. Storage stability test of lignin-modified binders

3.5 Production of Asphalt Mixes with Lignin-Modified Binder

In this study, the properties and performances of the asphalt mixes prepared with Lignin-modified binders were evaluated at Louisiana State University (LSU) and University of Oklahoma (OU). The LSU team selected a commonly available Louisiana asphalt mix and modified with lignin-modified binder. The cracking and moisture-induced damage resistance of the asphalt mix were evaluated by the LSU team. At OU, a commonly used Oklahoma asphalt mix was produced with lignin-modified binders. The rutting and cracking resistance of the asphalt mix was evaluated by the OU team. The following section presents the details of the asphalt mix production at LSU and OU.

3.5.1 Collection of Materials to Produce Asphalt Mixes at LSU

A Job Mix Formula (JMF) for a surface mix that was approved by the Louisiana Department of Transportation and Development (LaDOTD) was selected as the LSU control mix. This mix has been used in road construction projects around the Baton Rouge area. The surface mix consisted of four aggregate types, namely Vulcan #78, Vulcan #11, sand aggregate #10, and RJ Daigle Reclaimed Asphalt Pavement (RAP). The mix design included 36.3% Vulcan #78, 29.7% Vulcan #11, 15% sand aggregate #10, and 19% RJ Daigle RAP by weight (see Table 2). The gradations of the aggregates are presented in Table 3. Approximately 1% of the asphalt binder was contributed by the RAP material.

The research team at LSU coordinated with LaDOTD and a contractor in Geismar (Louisiana) to collect the necessary aggregates for the purpose of the study. An illustration of the asphalt mix production plant is provided in Figure 9.

Table 2. Amounts of aggregates used to produce asphalt mix at LSU

Aggregate	%Used
Vulcan #78	36.3
Vulcan #11	29.7
Sand	15.0
RAP	19.0

Figure 9. An illustration of the asphalt mixture production plant in Louisiana

Table 3. Aggregate gradation for asphalt mix used by LSU team

	%Passing			
Sieve Size (in.)	Vulcan 78 (%)	Vulcan 11 (%)	Sand (%)	RAP (%)
3/4"	100.0	100.0	100.0	100.0
1/2"	86.6	100.0	100.0	96.1
3/8"	60.4	99.9	100.0	91.0
No. 4	11.5	92.6	94.4	70.8
No. 8	2.2	70.0	81.4	47.0
No. 16	1.6	60.0	61.6	29.2
No. 30	1.5	50.0	50.0	28.0
No. 50	1.4	36.0	20.0	8.8
No. 100	1.0	20.0	0.6	3.0
No. 200	0.65	15.00	0.1	3.00

3.5.2 Collection of Materials to Produce Asphalt Mixes at OU

An approved Oklahoma Department of Transportation (ODOT) S4 mix design with a Nominal Maximum Aggregate Size (NMAS) of 12.5 mm, was selected by the OU team in consultation with ODOT's Asphalt Branch Manager. This mix design was modified to incorporate 5% and 10% lignin-modified binder. Necessary materials, such as aggregates, asphalt binder, Reclaimed Asphalt Pavement (RAP) and rejuvenators required for this study were collected by contacting the material suppliers. Aggregates were collected from Silver Star Construction Co. and Haskell Lemon Construction (Figure 10). The fine RAP used in this study was collected from Silver Star Construction Co. (Figure 11). The mineral aggregates consisted of 5/8-inch (15.875-mm) crushed stone chips, manufactured sand, 3/16-inch (4.76-mm) screenings and local sand. A PG 67-22 binder modified with lignin was prepared and sent by Louisiana Tech was used for this purpose. A rejuvenator from Cargill Anova was collected for the purpose of this study. The proportions of different aggregates used in producing the asphalt mix is shown in Table 4. Gradations of the individual mineral aggregates are presented in Table 5 along with the ODOT requirements for an asphalt mix with a NMAS of 12.5-mm. The amount of asphalt binder used in the ODOT approved design was 5.2%. The amount of asphalt binder was adjusted to incorporate 5% and 10% lignin in the asphalt mix.

Figure 10. Collection of aggregate by OU team for the study

Figure 11. Fine RAP sampled at Silver Star Construction Co., OK

Table 4 Amounts of aggregates used to produce asphalt mix at OU

Aggregate	%Used
5/8-inch (15.875-mm) Crushed Stone Chips	28
Manufactured Sand	20
3/16-inch (4.76-mm) Screenings	22
Local Sand	10
Fine RAP	20

Table 5 Gradation of aggregates collected by OU team

	Percent Passing (%)						
Sieve	5/8" Chips	3/16" Screens	Manufactured Sand	Sand (GMI)	Fine RAP	Combined Gradation	ODOT Requirements
3/4"	100	100	100	100	97	99	100
1/2"	70	100	100	100	93	90	100
3/8"	40	100	100	100	89	81	74-85
No. 4	5	94	86	94	71	63	56-70
No. 8	2	67	52	91	54	45	40-60
No. 16	2	47	35	88	41	35	31-39
No. 30	2	34	27	80	24	26	22-30
No. 50	1	24	23	43	23	19	16-23
No. 100	1	17	21	43	15	16	13-19
No. 200	1.3	12.0	12.0	1.5	9.5	7.5	6-9

3.5.3 Preparation of Asphalt Mixes with Lignin-Modified Binder

To prepare the asphalt mixes, aggregate blends were prepared by combining the necessary amounts of different aggregates. The lignin-modified binder and aggregates were then heated in the oven at 163°C for two hours. It was observed that the lignin settles down at the bottom of the can during the heating process. Therefore, before adding to the aggregate blend, the binder was mixed for few minutes using a high-shear mixer to keep the lignin suspended in asphalt binder. The heated aggregates were taken out of the oven and the required amount of heated binder was added to the aggregate blend and mixed using a mixer. As mentioned earlier, asphalt mixes with 0% (control mix), 5% and 10% lignin-modified binders were produced at LSU and OU.

At OU, one of the asphalt mixes with 10% lignin-modified binder was produced with rejuvenator. In that case, the rejuvenator was added to the asphalt binder before mixing with the aggregate blend. The amount of rejuvenator used in this asphalt mix was 2.1% by the weight of the neat binder. Figure 12 shows the preparation of asphalt mixes with lignin-modified binder.

Figure 12. Preparation of asphalt mixes with lignin-modified binder

3.6 Performances of Asphalt Mixes with Lignin-Modified Binder

3.6.1 Air Void Contents of Asphalt Mix Specimens

In this study, the target air void content for all prepared specimens was set at 7.0 ± 0.5%. In order to verify the achieved air void, the theoretical maximum specific gravity (G_{mm}) and the bulk specific gravity (G_{mb}) were determined. The amount of loose mixture used in the compaction process was calculated based on G_{mm}, G_{mb}, and the diameter of the specimens. The theoretical maximum specific gravity (G_{mm}) was determined according to AASHTO T 209 (AASHTO, 2022). The minimum mass of the sample is dependent on the Nominal Maximum Aggregate Size (NMAS). In order to determine the G_{mm}, two set of loose mixes were prepared for each mix type. The G_{mm} was calculated using Equation 6 for each mix. The bulk specific gravity was calculated using Equation 7. After determining the G_{mm} and G_{mb}, the air void content for each test specimen was calculated using Equation 8.

$$G_{mm} = \frac{A}{A-(C-B)}$$

Equation 6

Where,

A = mass of dry sample in air (gram);
B = mass of the pycnometer under water (gram); and
C = mass of sample and pycnometer under water (gram).

$$\mathrm{G_{mb}} = \frac{\textit{weight in the air}}{\text{SSD weight} - \text{Weight in water}}$$

Equation 7

$$\text{Air Void (\%)} = \frac{\mathrm{G_{mm}} - \mathrm{G_{mb}}}{\mathrm{G_{mm}}} * 100$$

Equation 8

3.6.2 Indirect Tensile Asphalt Cracking Test (IDEAL-CT) to Evaluate Cracking Resistance

In this study, the IDEAL-CT tests were conducted to determine the Cracking Tolerance Index (CT_{index}) following the ASTM D8225 (ASTM, 2022) test method to evaluate the cracking resistance of the asphalt mixes. Also, the Indirect Tensile Strength (ITS), failure energy and post peak slopes of the asphalt mixes were determined. To accomplish this goal, asphalt mix specimens with a diameter of 150 mm and heights of 62 mm were produced in the laboratory using Superpave Gyratory Compactor (SGC). For this purpose, the loose mix was placed in the oven for 4 hours at 135°C. Then the loose mix was heated at compaction temperature (149°C) for another 30 minutes and the specimens were molded. To calculate the CT_{index} of asphalt mixes, the IDEAL-CT tests were performed on the compacted specimens by applying a vertical monotonic load at a rate of 50 mm/min until failure. An MTS loading system was used to collect the load and displacement data during testing (Figure 13 (a) and 13 (b)).

(a) (b)

Figure 13. IDEAL-CT test on asphalt specimen for cracking resistance of asphalt mixes: (a) test setup and (b) specimen after test

A typical load-displacement curve is shown in Figure 14. The ITS was calculated by dividing the peak load with cross-sectional area. The CT_{index} (Equation 9) of a specimen was calculated as a function of total failure energy (G_f) and the slope of the post-peak curve at 75 percent of the peak load (m_{75}), following the ASTM D8225 test method (ASTM, 2022). The G_f required for the CT_{index} calculation was determined using Equation 10. The higher the CT_{index} the better the cracking resistance of an asphalt mix.

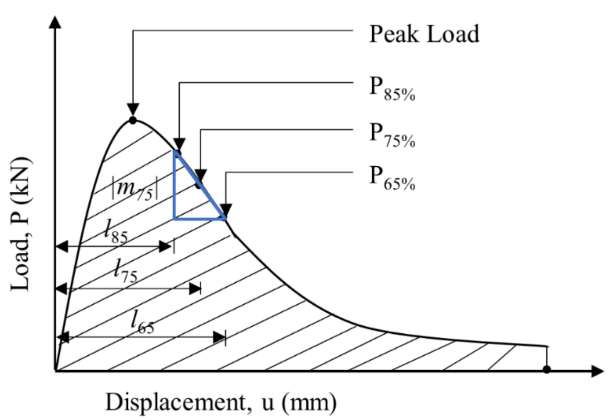


Figure 14. Typical load-displacement diagram for CT_{index} calculation

$$CTindex = \frac{t}{62} * \frac{l_{75}}{D} * \frac{G_f}{|m_{75}|} * 10^6$$ **Equation 9**

$$G_f = \frac{W_f}{D*t} * 10^6$$ **Equation 10**

where,

CT_{index} = Cracking Tolerance index;
G_f = Failure Energy (Joules/m^2);
W_f = Work of failure, area under the load-displacement curve (Joules);
m_{75} = post-peak slope at 75% of peak load (N/m);
l_{75} = displacement at 75% of peak load (mm);
D = Specimen diameter (mm); and
t = Specimen thickness (mm).

3.6.3 Hamburg Wheel Tracking (HWT) Test to Evaluate Rutting Resistance

The HWT test was conducted on laboratory compacted asphalt mix specimens in accordance with the AASHTO T 324 (AASHTO, 2022) test method to determine their rutting susceptibility. For this test, loose mixes were aged in the oven for two hours at the compaction temperature prior compaction following the short-term oven aging condition. The diameter and height of the compacted specimens were 150 mm and 62 mm, respectively. The compacted specimens with air voids of 7 ± 0.5% were used for testing. The HWT tests were conducted at 50°C with a wheel pass frequency of 52 passes/minute (Figure 15). The load on the wheel was 705 N (158 lbs.). The tests were terminated after reaching a maximum rut depth of 20 mm or 20,000-wheel passes, whichever reached first. The HWT data were analyzed using both AASHTO T 324 (AASHTO, 2022) and Texas A&M University (TAMU) method to evaluate rutting and moisture-induced damage resistance of the mixes (Yin et al., 2014).

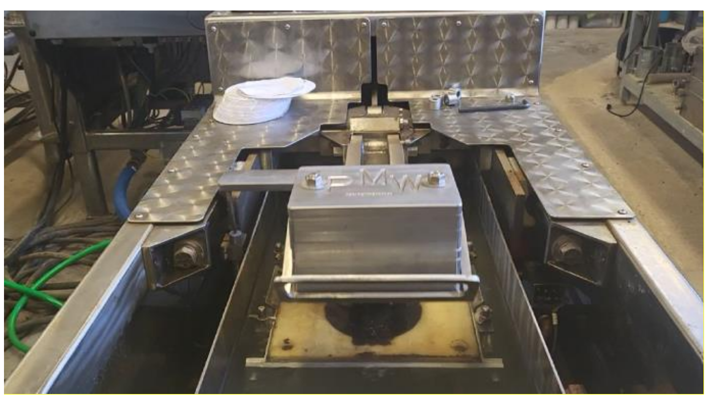


Figure 15. Hamburg Wheel Tracking test for evaluating rutting resistance of asphalt mixes

3.6.4 Modified Lottman Test to Evaluate Resistance to Moisture-Induced Damage

Moisture-induced damage is one of the most significant forms of asphalt pavement deterioration in Louisiana, significantly reducing the performance and service life of asphalt pavements. When water infiltrates the pavement, it weakens the bond between the asphalt binder and aggregate particles, leading to reduced structural integrity. The resistance of the surface mixes to moisture-induced damage was evaluated using the modified Lottman test, as outlined in AASHTO T 283 (AASHTO, 2022). This test determines the Tensile Strength Ratio (TSR) by calculating the ratio of the average Indirect Tensile Strength (ITS) of three wet-conditioned specimens to the average ITS of three dry-conditioned specimens. Figures 16(a) and 16(b) shows an asphalt specimen during and after subjected to modified Lottman test. One freezing and thawing cycle was applied for the wet-conditioned specimens. Both wet- and dry-conditioned specimens were submerged in a 25°C water bath for two hours before testing. The TSR values of the asphalt mixes were calculated using Equation 11.

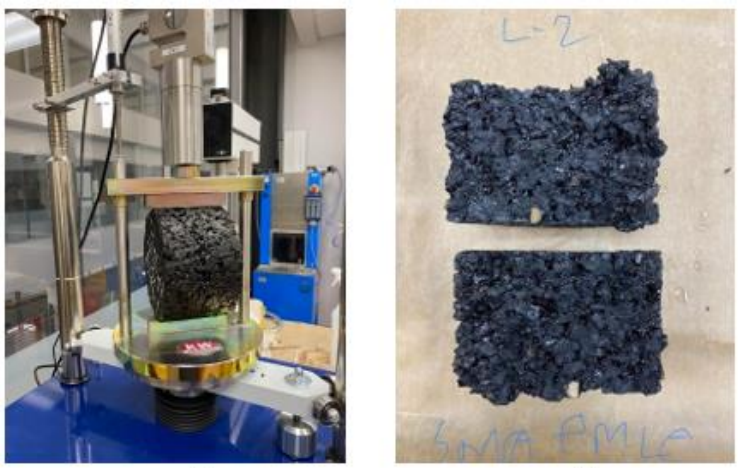
$$TSR = \frac{s_{t,wet}}{s_{t,dry}}$$

Equation 11

where,

$s_{t,wet}$= the average indirect tensile strength of the wet-conditioned specimen, and
$s_{t,dry}$= the average indirect tensile strength of the dry-conditioned specimen.

The TSR of each mix was compared against the minimum recommended value of 0.8 specified by Louisiana standards, providing a benchmark for predicting the resistance to moisture-induced damage of the mixes prepared with lignin-modified binders.



(a) (b)

Figure 16. Modified Lottman test: asphalt mix specimen (a) during and (b) after test

Chapter 4. Results and Discussions

4.1 Characterization of Lignin

4.1.1 Particle Size Distribution

The Hydrothermal Carbonization (HTC) treatment was used by the Louisiana Tech University team to produce lignin from rice husks. It was found that, with HTC treatment, 75 grams of raw rice husks can produce 30 to 35 grams of lignin, resulting in a yield of 40-50%. Also, the HTC treatment process changed both the chemical and physical properties of the rice husk. Figures 17(a) and 17(b) show the photos of untreated rice husks and produced lignin, respectively. The rice husks became powder after HTC treatment. The particle size distributions of the rice husk before and after and HTC treatment are shown in Table 6. It is evident that the size of the particles reduced significantly after HTC treatment. The bulk density of rice husks and lignin were found to be 145 kg/m^3 and 265 kg/m^3, respectively.

Table 6. Change in particle size distribution before and after HTC treatment

US Mesh	Particle size (mm)	Before HTC	After HTC
14	1.41	78%	5%
20	0.841	21%	13%
25	0.707	1%	16%
40	0.4	1%	42%
80	0.177	0%	19%
Residue	< 0.177	0%	5%

(a) (b)

Figure 17. (a) Raw rice husk and (b) rice husk derived lignin

4.1.2 Fourier Transformed Infrared (FTIR) Spectrometer

Figure 18 shows the FTIR spectra of the untreated rice husk, RH 220 and RH 250.
The vibration peak at 896 cm^{-1} signifies C_1−H deformation associated with a ring vibration in amorphous cellulose (Raj et al., 2015). The vibrational peak at 1162 cm^{-1} signifies C-O-C

vibrations arising from the amorphous stretching of cellulose types I and II (Arora et al., 2020). The cellulose and hemicellulose constituents in are shown by the wavenumbers at 1315 cm^{-1} and 1425 cm^{-1}, corresponding to CH_2 bending and CH asymmetric deformation, respectively (Haque et al., 2020). The identification of a vibrational peak at a wavenumber of 1515 cm^{-1} signified the skeletal stretching of the aromatic ring in lignin. In rice husk, the Si–O–Si antisymmetric stretch and C–O stretch are identified by peaks observed at 1100–1000 cm^{-1} and 1065–1015 cm^{-1}, respectively (Hossain et al., 2020). The peak at 1600 cm^{-1} signifies the C=O stretching associated with the aromatic ring vibration of lignin (Li et al., 2015).

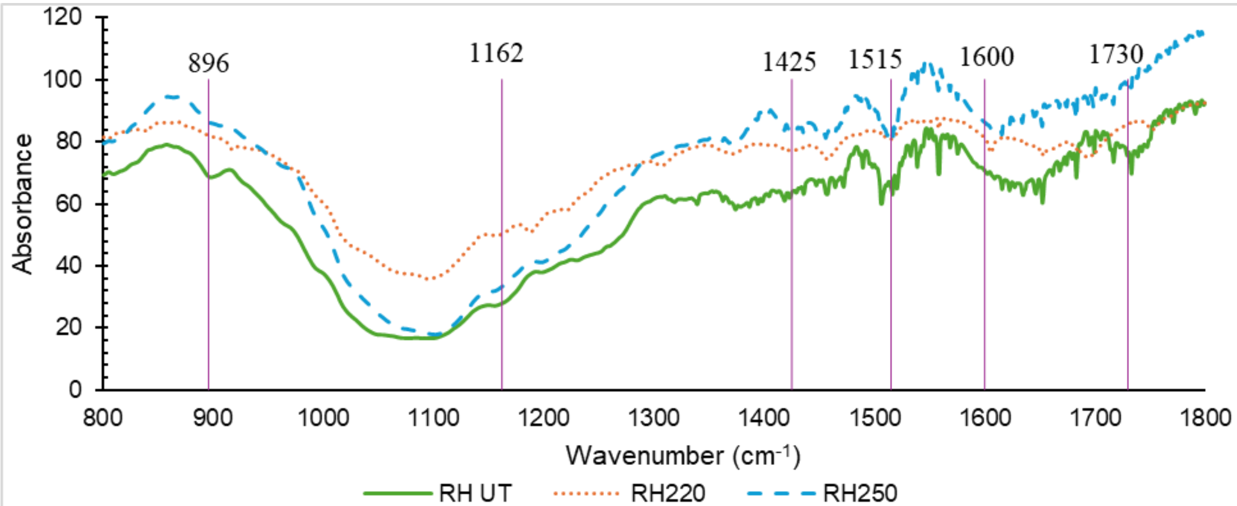


Figure 18. FTIR spectra of raw rice husk and rice husk derived lignin

4.1.3 Lignin Content of Rice Husk

Figure 19 shows the Acid Insoluble Lignin (AIL) contents of the HTC treated lignin compared to the untreated rice husk. Lignin was produced at two different HTC temperatures, namely 220℃ and 250℃. For the convenience of this report, the lignin derived from rice husks at 220℃ and 250℃ are denoted as RH 220 and RH 250, respectively. To ensure repeatability, three specimens were tested for each sample. In Figure 19, the HTC treatment substantially extracted acid insoluble lignin from rice husk. Compared to an HTC treatment at 220℃, the lignin yield is significantly higher at 250℃. Therefore, the HTC operating temperature was set at 250℃ for the reminder of the project.

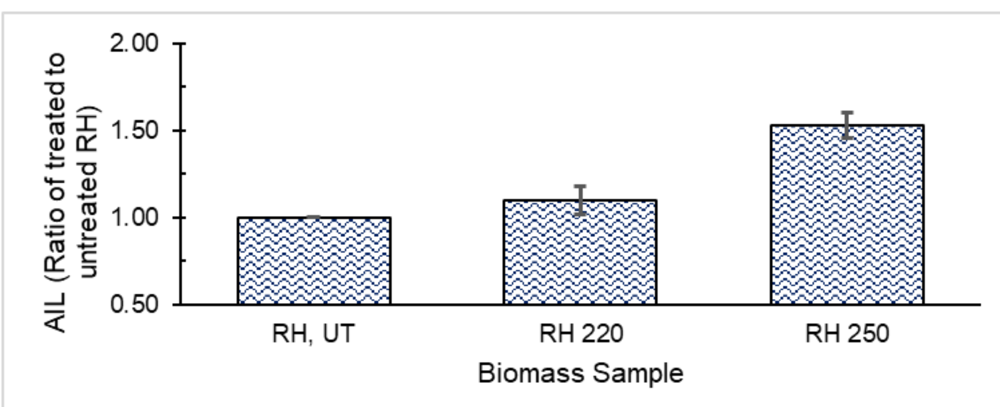


Figure 19. Acid Insoluble Lignin (AIL) in rice husk before and after HTC treatment

Figure 20 presents the Acid Soluble Lignin (ASL) content before and after HTC treatment. From Figure 20, a decrease in the ASL content was observed after HTC treatment. The high pressure and temperature during HTC can lead to polymerization and condensation in lignin molecules. The AIL fraction may have increased as these processes created larger and more complex lignin structures that are less soluble in acid. Also, during the HTC process, the soluble fraction of lignin, which contained smaller and less complicated lignin fragments may have thermally broken down. Therefore, the HTC treatment resulted in an increase in the AIL content while a decrease in the ASL content. As the contribution of ASL is much lower compared to the AIL, an overall increase in lignin content was observed after the HTC treatment.

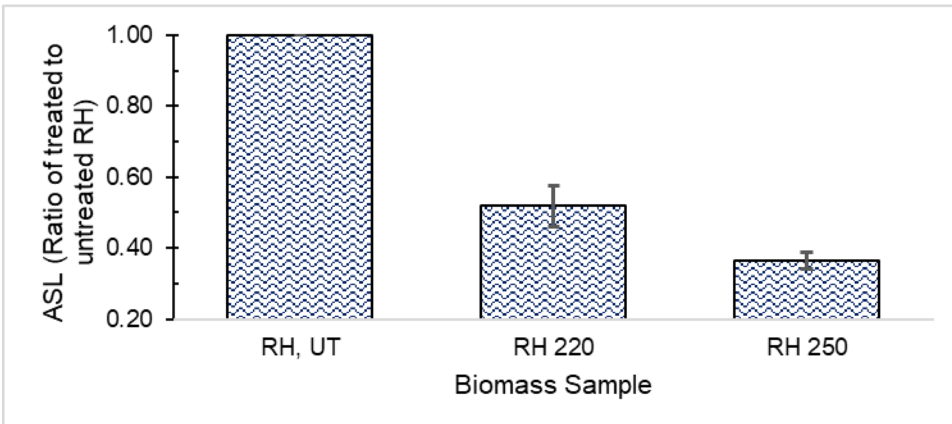


Figure 20. Acid Soluble Lignin (ASL) in rice husk before and after HTC treatment

4.1.3 Higher Heating Value (HHV) of Combustion

Figure 21 shows the HHV values of treated and untreated rice husks (obtained from bomb calorimeter). The HHV value increased after HTC treatment. Also, the HHV value was found to increase with an increase in the HTC treatment temperature. The higher calorific value of lignin compared to cellulose and hemicellulose suggests an increase in lignin content following HTC treatment. The results indicate that the HTC treatment at 250°C is more effective for lignin extraction compared to the treatment at 220°C.

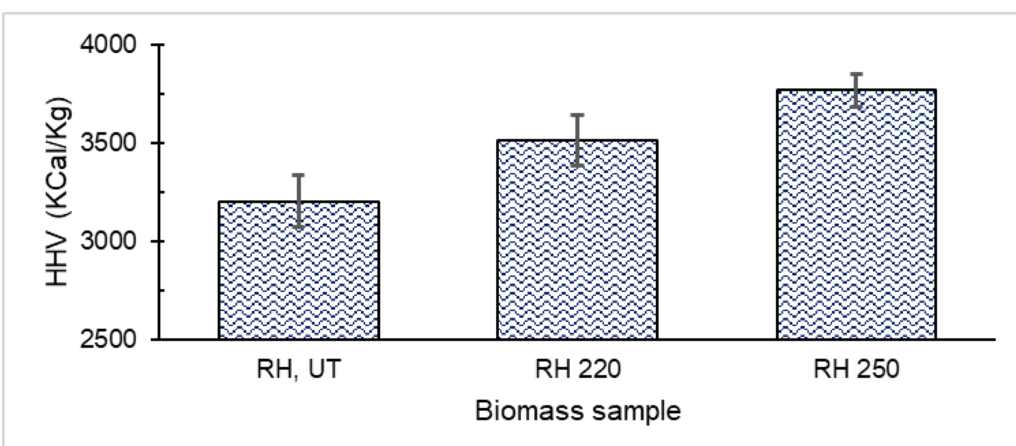


Figure 21. HHV of treated and untreated rice husk

4.1.5 Melting Point of Lignin

A Differential Scanning Calorimeter (DSC) was utilized to measure the melting point of rice husk derived lignin. Three lignin samples were tested using DSC for this purpose. Figure 22 shows the results of the DSC test. It was observed that the average melting point is 258.9°C with a standard deviation of 17.4°C. The results indicate that the lignin is not expected to melt during mixing with binder at 170°C.

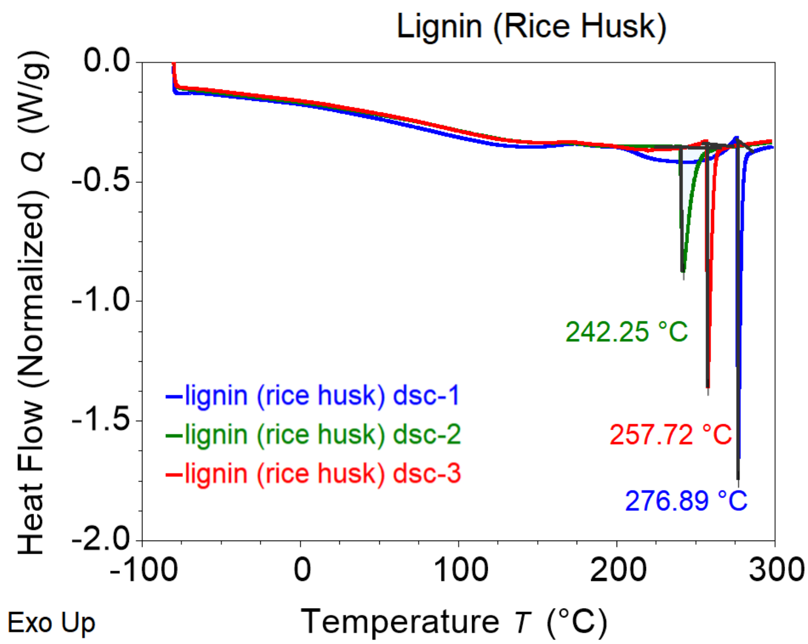


Figure 22. Differential Scanning Calorimeter (DSC) thermograms of rice husk derived lignin

4.2 Characterization of Lignin-Modified Asphalt Binder

4.2.1 High-Temperature Performance Grade

The high-temperature continuous grades of both unaged and aged neat and lignin-modified binders were determined using DSR tests. Figure 23 shows the values of the rutting factor, G*/sinδ for neat PG67-22 and lignin-modified PG67-22 (5% and 10% modification) at 70°C, 76°C, and 82°C temperatures. It was found that the G*/sinδ increases with an increase in the lignin content in the binder. For example, at 70°C, the G*/sinδ for the PG67-22 was 0.94 kPa, which increased to 1.24 kPa and 1.30 kPa with the addition of 5% and 10% lignin, respectively. This observation indicates that the lignin modification of the binder enhances its resistance to rutting.

The continuous performance grades of the tested binders were determined using AASHTO M320 (AASHTO, 2022) specification. Table 7 shows the continuous high-temperature PG of unaged and RTFO-aged neat and lignin-modified PG67-22 binders. The lowest value among the continuous PGs of the unaged and RTFO-aged binders was used as the high-temperature PG of the binder. The addition of 5% and 10% lignin was found to increase the high-temperature PG of the neat binder. The continuous PG of the PG67-22 binder without lignin modification was 69.3°C, whereas the addition of 10% lignin increased the continuous PG to 71.4°C.

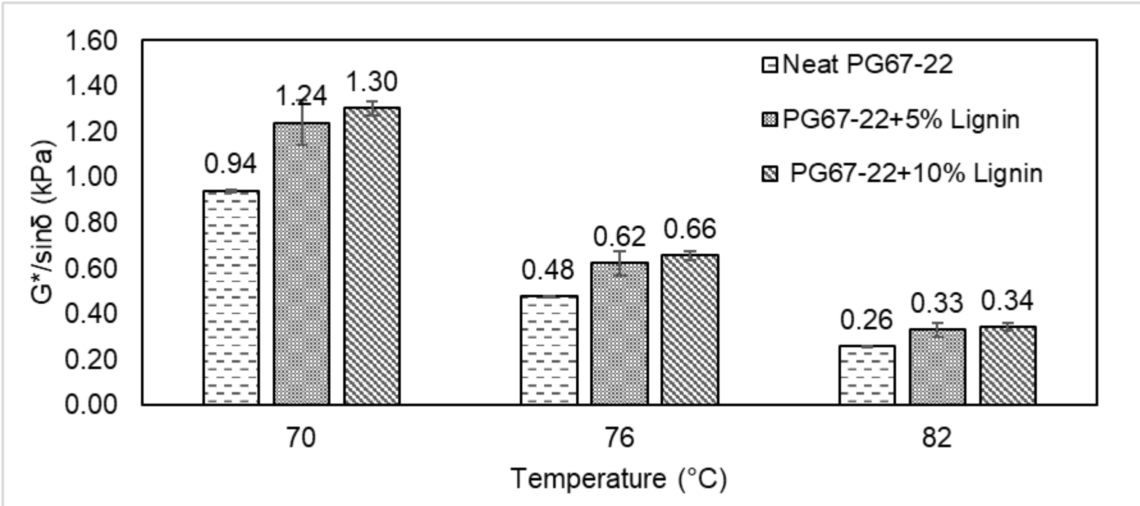


Figure 23. Variation of G*/sinδ with temperature for lignin-modified binders

Table 7. High-temperature continuous PG of lignin-modified binders

Name of binders	Temperature (°C)	High-temperature PG (°C)
Unaged PG67-22	69.3	69.3
RTFO-aged PG67-22	69.9	69.3
Unaged PG 67-22+5%Lignin	71.4	70.9
RTFO-aged PG 67-22+5%Lignin	70.9	70.9
Unaged PG 67-22+10%Lignin	71.4	71.4
RTFO-aged PG 67-22+10%Lignin	71.9	71.4

4.2.2 Low-Temperature Performance Grade

Figure 24 shows the stiffness (S) values of the lignin-modified binders from the BBR tests at -6°C, -12°C and -18°C. As expected, the S-value was found to increase as the temperature reduced from -6°C to -18°C. Also, from Figure 24, it was observed that the stiffness of the binder increased with an increase in the lignin content. For example, at -6°C, the S-value for the neat PG67-22 binder was found to be 69 MPa, whereas the addition of 5% and 10% lignin increased the S-value to 74 and 112 MPa. Similar trends were observed at other test temperatures. The results indicate that the pavement constructed with lignin-modified binder possesses higher susceptibility to low-temperature cracking than the neat binder.

The rate of stress relaxation (m-value) from the BBR test represents a binder's ability to dissipate stress. Figure 25 presents the m-values of the lignin-modified binders from the BBR tests. At -6°C, the m-value of the 5% and 10% lignin-modified binders were found to be same as the neat PG67-22. However, m-values for the lignin-modified binders were found to be lower than the neat binder at -12°C and -18°C. A lower m-value signifies a slower relaxation of thermal stresses, which can negatively impact the performance of asphalt pavements at low temperatures. The increased stiffness and decreased m-value was found to negatively impact the low-temperature properties as well as low-temperature PG grades of the lignin-modified binders. Figure 26 shows the changes in the continuous low-temperature PG with the addition of lignin. It was observed that the addition of 5% and 10% lignin to PG67-22 binder changed the low-temperature PG from -23.4°C to -22.9°C and -20.0°C, respectively.

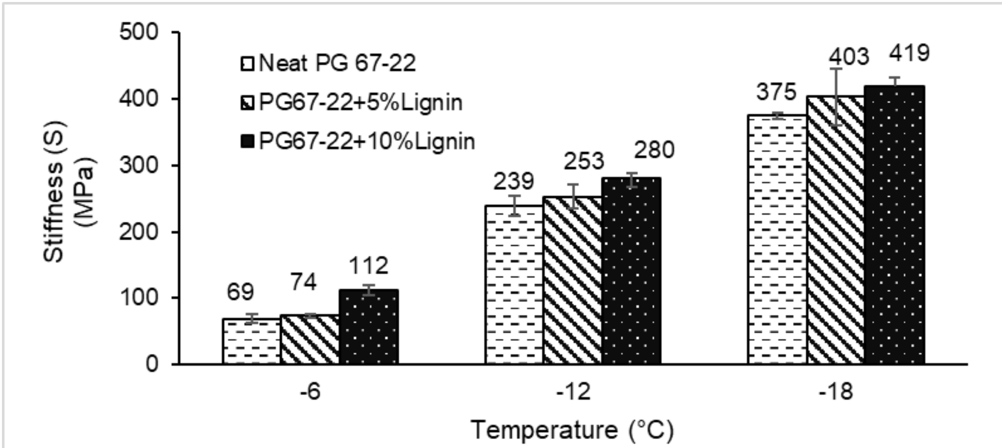


Figure 24. Low-temperature stiffness of lignin-modified binders at different temperatures

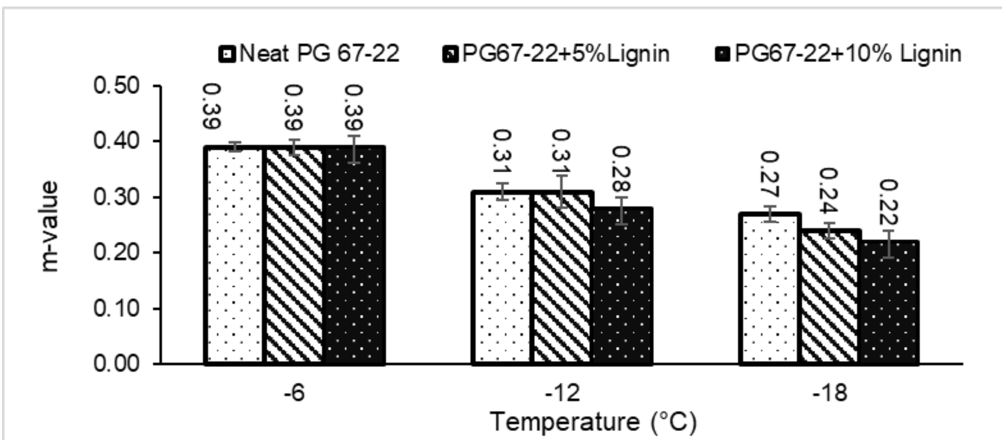


Figure 25. Low-temperature m-values of lignin-modified binders at different temperatures

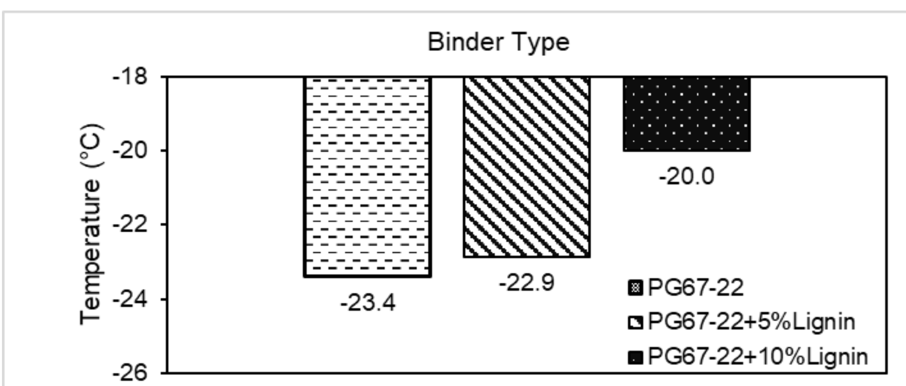


Figure 26. Low-temperature PGs of lignin-modified binders

4.2.3 Intermediate-Temperature Performance Grade

The DSR test was conducted on the PAV-aged 0% and 10% lignin-modified asphalt binders at intermediate temperatures to evaluate their resistance to fatigue cracking. The fatigue parameters (G*. sin δ) of the binders were determined from the DSR test and compared. The G*. sin δ value of 0% and 10% lignin-modified asphalt binders were 6,573 kPa and 5,038 kPa at their corresponding intermediate temperature. A G*. sin δ value less than 5,000 kPa is required to limit stiffness and reduce potential for fatigue cracking in asphalt binder. As the neat PG67-22 binder exhibited a G*. sin δ value greater than 5,000 kPa, it is expected that the asphalt mixes with lignin-modified binders will exhibit poor resistance to cracking.

4.2.4 Non-Recoverable Creep Compliance (J_{nr}) and %Recovery of Lignin-Modified binders

The data obtained from the MSCR test was used to determine the nonrecoverable creep compliance (J_{nr}) and %Recovery of lignin-modified binders. The %Recovery measures the elastic response of a binder and shows its potential to return to its original configuration after deformation [15,16]. Table 8 shows the J_{nr} and %Recovery of lignin-modified binders. It was observed that the addition of the lignin has resulted in a slight improvement in the %Recovery at both 0.1 kPa and 3.2 kPa stress levels. The 10% lignin-modified binder exhibited the highest %Recovery values. The J_{nr} value indicate the deformation response of a binder to cyclic loading [17]. The lower the J_{nr} value, the better the rutting resistance. From Table 8, the lignin modification had lowered the J_{nr} value at both stress levels compared to the neat binder indicating better resistance to rutting with the addition of lignin to neat binder.

Table 8. The %Recovery (left) and J_{nr} (right) of the lignin-modified binders at 64°C

Binder Name	0.1 kPa	3.2 kPa	0.1 kPa	3.2 kPa
PG 67-22	0.00	0.22	4.61	5.21
PG 67-22 +5% Lignin	0.11	0.53	3.30	3.51
PG 67-22 +10% Lignin	3.38	0.34	3.12	3.57

4.2.5 Rheological Master Curve

Rheological master curves are often produced to understand the effects of binder modification at broad temperature regions. Figure 27(a) shows the complex modulus master curves of the neat and 5% lignin-modified PG67-22 binders. Also, the phase angle, storage modulus and loss modulus master curves are presented in Figure 27(b). Figures 27(a) and 27(b) indicate that the complex modulus, phase angle, storage modulus and loss modulus values are similar to the neat binder over broad temperature ranges. Therefore, the properties of the lignin-modified binders are expected not to show significant changes over broader temperature ranges from neat binder.

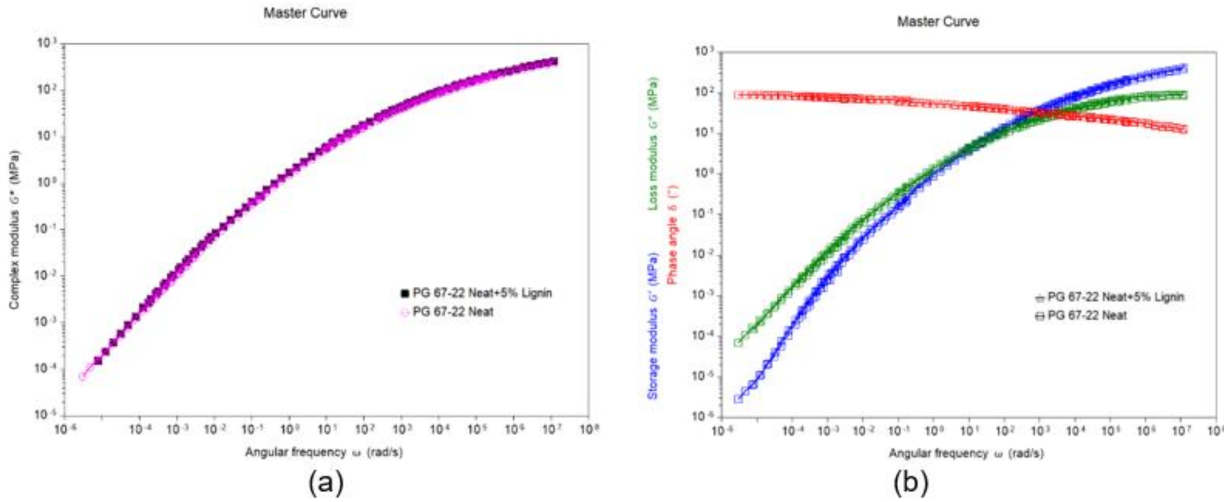


Figure 27. Rheological master curves of neat and lignin-modified binders; (a) complex modulus; (b) phase angle, storage modulus and loss modulus master curves

4.2.6 Storage Stability of Lignin-Modified Binder

To assess the homogeneity and performance of lignin-modified binders during storage, transportation and application, the storage stability test was conducted using the ASTM D7173 (ASTM, 2022) test method. In this study, the variations in G* values between the top and bottom layers of binder samples were compared to determine the storage stability of the lignin-modified binders. A stability index based on the ratio of the G* values of the top and bottom layer binder samples was determined to assess the stability of the binders [18]. A stability index closer to 1 will indicate less variation and more favorable thermal stability. Table 9 presents the stability index of the binder samples at 70°C, 76°C and 82°C.

From Table 9, it is evident that the addition of 10% lignin could result in significantly poor stability index values. The stability indices for the 10% lignin-modified binder were found to be 0.44, 0.46 and 0.46 at 70°C, 76°C and 82°C, respectively. The results indicate that the 10% lignin modification may result in phase separation between binder and lignin and cause unstable condition. The binder with 5% lignin modification exhibited better stability index values compared to the 10% lignin modification. The 5% lignin-modified binder has exhibited a stability index value of 0.68 at 76°C.

In this study, the effect of the reduction in lignin particle size on the stability of the binder was investigated and presented in Table 9. The reduction in particle size was found to positively influence the stability of the lignin-modified binder. For 5% lignin modification, an increase in the stability index value from 0.68 to 0.76 at 76°C was observed with reduced particle size. The results suggest a direct correlation between particle size and thermal stability. Also, to examine the potential ways of enhancing storage stability of the lignin-modified binder, 1% SBS polymer, by weight of the binder, was incorporated utilizing a high shear mixing method. The inclusion of SBS significantly augmented the stability of the lignin-modified binder. Specifically, the 10% lignin modification combined with a 1% SBS resulted in an increase in the stability index value from 0.46 to 0.72 at 76°C. Additionally, for the 5% reduced size lignin-modified binder, the incorporation of 1% SBS increased the stability index value from 0.76 to 0.91 at 76°C. Based on the results of the storage stability test, it can be inferred that the combination of PG67-22 with 5% reduced particle size lignin and 1% SBS is expected to exhibit the highest stability performance among all the binders. The binders can be ranked from most stable to least stable in the following order of 67-22 +5% Lignin (Reduced Size) +1% SBS, PG 67-22 +5% Lignin (Reduced Size), PG 67-22 +1% SBS +10% Lignin, PG 67-22 +5% Lignin and PG 67-22 +10% Lignin.

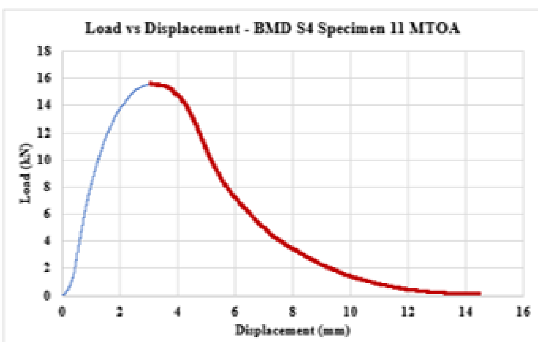
Table 9. Stability index of lignin-modified binders

Name of binder	**70** °C	**76** °C	**82** °C
PG 67-22 +5% Lignin	0.69	0.68	0.67
PG 67-22 +10% Lignin	0.44	0.46	0.46
PG 67-22 +1%SBS+10% Lignin	0.68	0.72	0.72
PG 67-22 +5% Lignin (Reduced Size)	0.75	0.76	0.76
PG 67-22 +5% Lignin (Reduced Size) +1%SBS	0.89	0.91	0.92

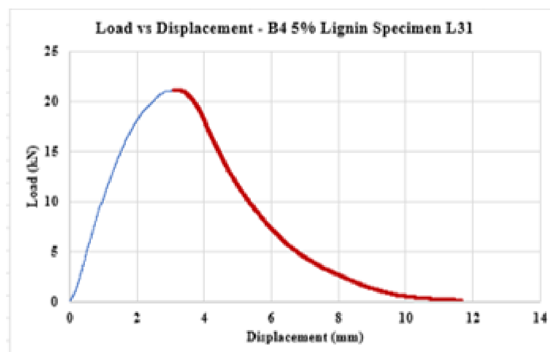
4.3 Characterization of Asphalt Mixes at OU

4.3.1 Indirect Tensile Strength (ITS) of Asphalt Mixes

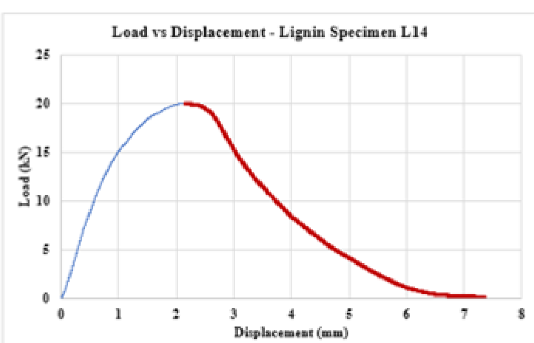
At OU, the Indirect Tensile Asphalt Cracking Test (IDEAL-CT) was conducted to determine the Indirect Tensile Strength (ITS), Failure Energy (G_f), post peak slope and CT_{index} of the asphalt mixes with lignin-modified binders. Figures 28(a), 28(b), 28(c) and 28(d) present the load-deflection curves obtained for asphalt mix specimen with 0% lignin, 5% lignin, 10% lignin, and 10% lignin with 2.1% rejuvenator, respectively.



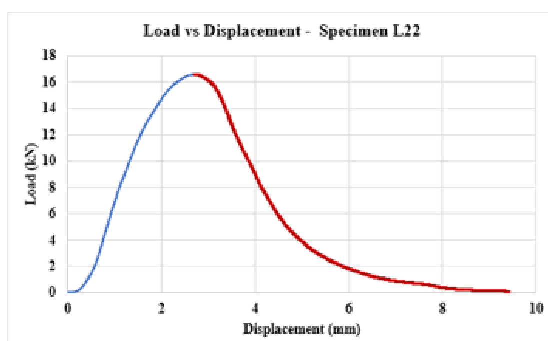
(a)



(b)



(c)



(d)

Figure 28. Load vs displacement curves from IDEAL-CT tests: (a) 0% lignin, (b) 5% lignin, (c) 10% lignin and (d) 10% lignin with 2.1% rejuvenator

The ITS values of the tested asphalt mixes are presented in Figure 29. Multiple specimens were tested to investigate the repeatability of the ITS values. The error bar in Figure 29 represents one standard deviation from average value. From Figure 29, it was observed that the asphalt mix with 0% lignin shows the lowest ITS value. The ITS value was found to increase with an increase in the lignin content. An increase in stiffness with the addition of lignin was responsible for the increase in ITS value. The result agrees with the binder test results as an addition of lignin was observed to increase the stiffness of the binder. An attempt was made to reduce stiffness with the addition of 2.1% rejuvenator. However, the addition of rejuvenator did not exhibit any significant change in the ITS value.

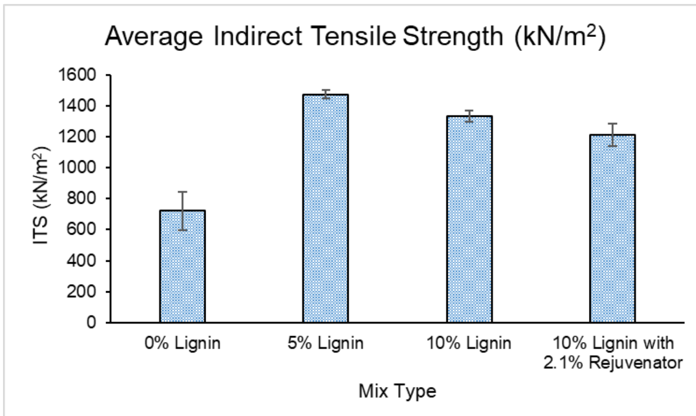


Figure 29. Average indirect tensile strength of asphalt mixes with lignin-modified binders

4.3.2 Failure Energy and Post peak Slope of Asphalt Mixes

The failure energy (G_f) and post peak slope (m_{75}) play important roles in determining the cracking resistance of asphalt mixes. The average failure energy and average post peak slope of the asphalt mixes are presented in Figures 30 and 31, respectively. From Figure 30, the failure energy was observed to increase with an increase in lignin content. The asphalt mix with 5% lignin showed the highest failure energy among other mixes. The use of rejuvenator was found to reduce the failure energy of the asphalt mix with 10% lignin-modified binders. From Figure 31, the post peak slope of the asphalt mix was found to increase significantly with the use of lignin-modified binders. A higher value of slope indicates a steeper post peak region and a brittle type of failure. Therefore, the asphalt mixes became stiffer and brittle with the use of lignin-modified binder. The use of rejuvenator was not found to reduce the post peak slope.

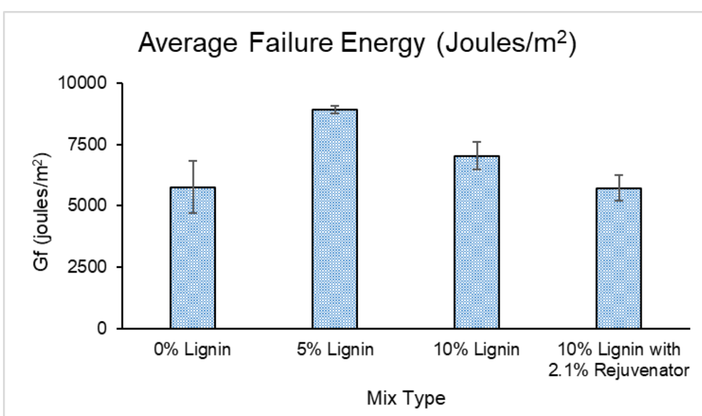


Figure 30. Average failure energy of asphalt mixes with lignin-modified binders

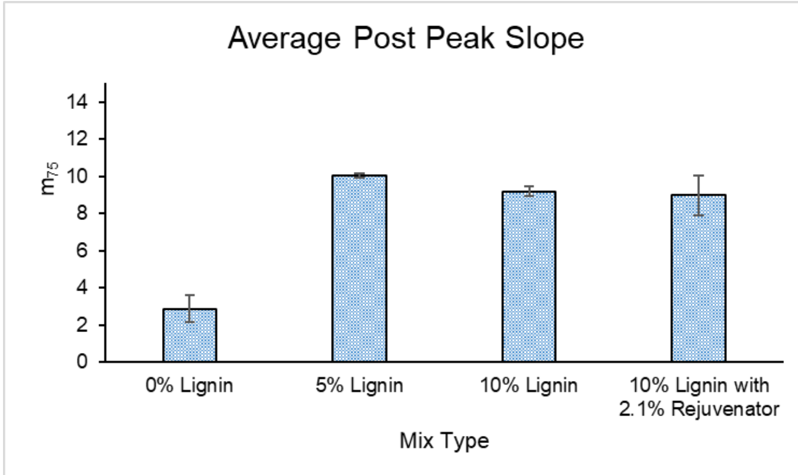


Figure 31. Average post peak slopes of asphalt mixes with lignin-modified binders

4.3.3 CT_{index} of Asphalt Mixes

Cracking resistances of the mixes were evaluated using the CT_{index} values from the IDEAL-CT tests. A summary of the IDEAL-CT test results is presented in Figure 32. The error bar in Figure 32 indicates one standard deviation from the average value. It was observed that the CT_{index} values decreased with an increase in the lignin. From Figure 32, it was observed that the asphalt mix with 0% lignin exhibited a CT_{index} value of 70 which then reduced to 43 and 17 with the addition of 5% and 10% lignin, respectively. As the neat PG67-22 binder exhibited a G*. sin δ value greater than 5,000 kPa, it was expected that the asphalt mixes with lignin-modified binders will exhibit poor resistance to cracking. The purpose of the addition of the rejuvenator was to improve the cracking resistance of the asphalt mix. However, Figure 32 shows no improvement in CT_{index} value with the addition of 2.1% rejuvenator to the asphalt mix with 10% lignin-modified binder. ODOT requires a CT_{index} value of 60 or higher for an intermediate BMD mix. None of the asphalt mix with lignin satisfied that criterion.

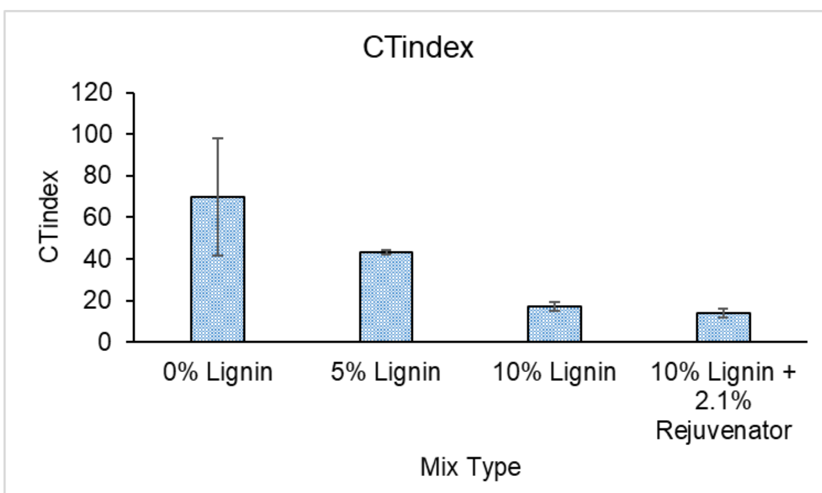
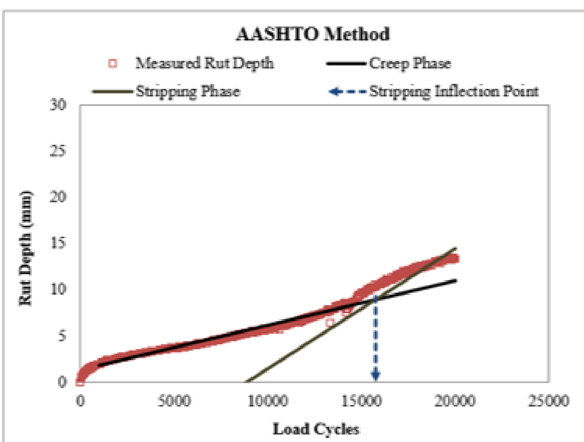


Figure 32. Average CT_{index} of asphalt mixes with lignin-modified binders

4.3.4 Rutting Resistance of Asphalt Mixes

The Hamburg Wheel Tracking (HWT) test was conducted to determine the rutting resistance of the asphalt mixes with lignin-modified binders. The HWT test results were analyzed using the AASHTO and Texas A&M University (TAMU) methods. Figures 33(a) and 33(b) shows the analysis of the HWT test results for asphalt mix with 0% lignin using AASHTO method and TAMU method, respectively. Similar results for asphalt mixes with 5% lignin, 10% lignin and 10% lignin + 2.1% rejuvenator are presented in Figures 34, 35 and 36, respectively. Summaries of the test results using AASHTO and TAMU methods are presented in Tables 10 and 4.6, respectively. A rut depth of 12.5-mm or less (at 10,000-wheel pass) is required by the ODOT BMD Special Provision for a mix with PG 64-22 binder (ODOT, 2023).

All the mixes were observed to exhibit satisfactory rutting resistance after 10,000-wheel passes. Also, the rutting resistance was found to improve with the addition of lignin. For example, the mix with 0% lignin exhibited a rut depth of 5.68 mm after 10,000-wheel passes, whereas the mixes with 5% and 10% lignin-modified binder exhibited 5.00 mm and 4.17 mm rut depths after 10,000-wheel passes, respectively. The addition of rejuvenator was found to produce similar rutting resistance as the asphalt mix with 10% lignin-modified binder. In the AASHTO method, the Stripping Inflection Point (SIP) from the HWT test is used as an indicator of moisture-induced damage resistance of an asphalt mix. A higher value generally indicates better resistance to moisture-induced damage. Both the mixes with 5% and 10% lignin-modified binders were observed to exhibit SIP at wheel passes higher than 15,000 indicating good resistance to moisture-induced damage. The Visco-plastic Strain at Stripping Number ($\Delta\varepsilon_{LC_{SN}}^{vp}$), Stripping Number ($LC_{SN}$) and Stripping Life ($LC_{ST}$) from the HWT tests were determined using the TAMU method and are presented in Table 11. All the mixes exhibited satisfactory $\Delta\varepsilon_{LC_{SN}}^{vp}$, LC_{SN} and LC_{ST} values. Overall, the mixes with lignin-modified binders satisfied the specifications for rutting and moisture-induced damage resistance for BMD mixes.



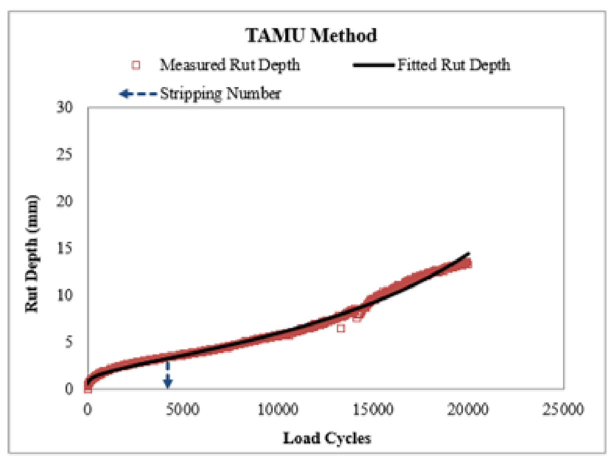
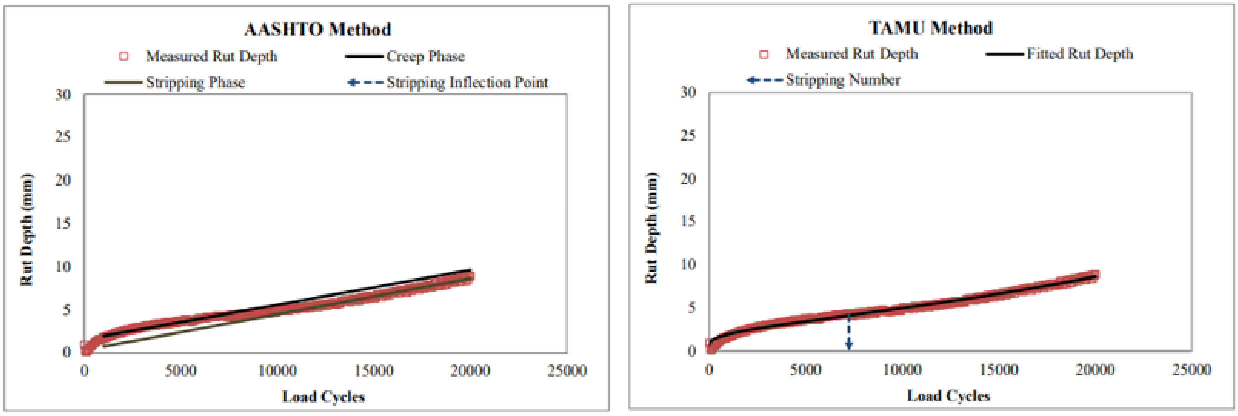
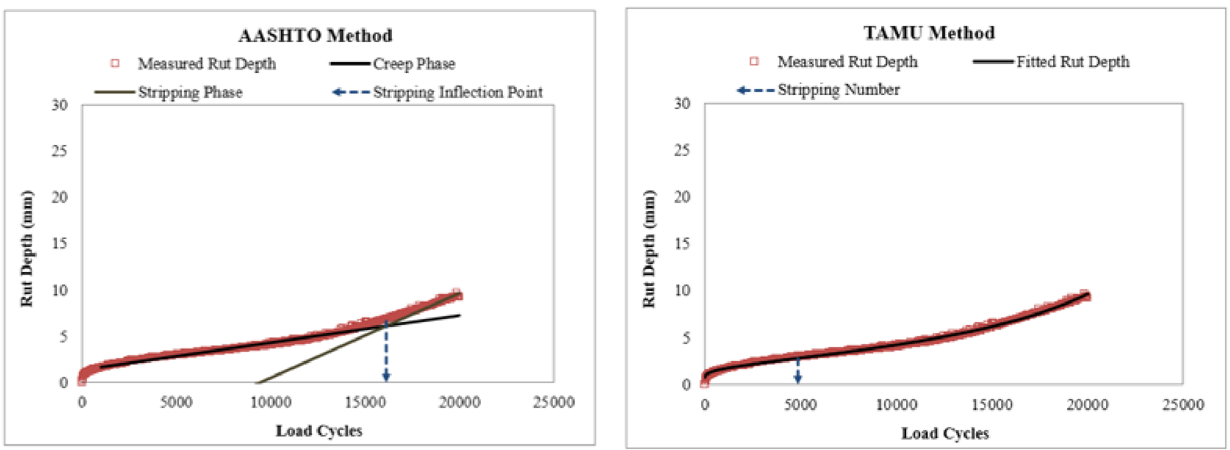


Figure 33. Analysis of HWT test results for asphalt mix with 0% lignin: (a) AASHTO method and (b) TAMU method



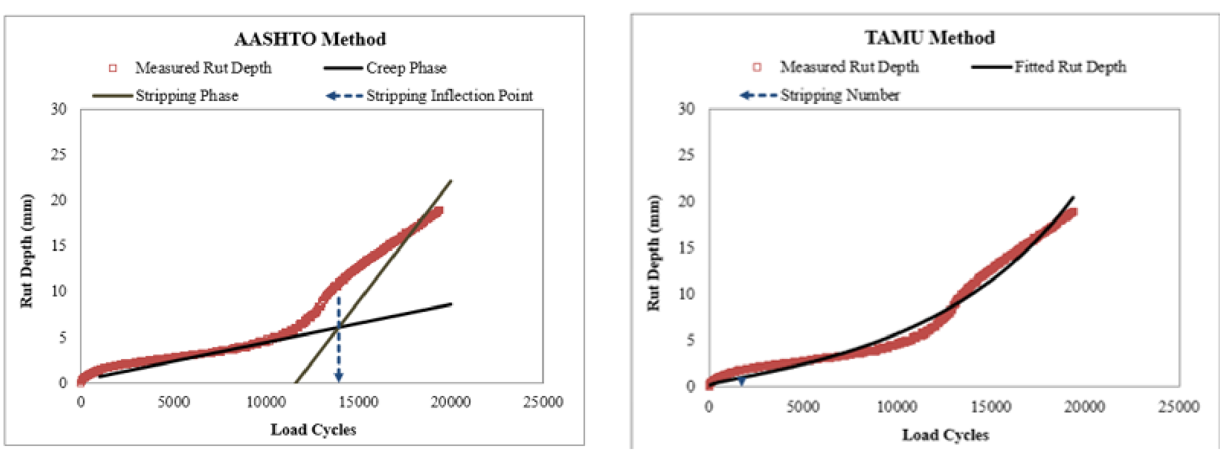
(a) (b)

Figure 34. Analysis of HWT test results for asphalt mix with 5% lignin-modified binder: (a) AASHTO method and (b) TAMU method



(a) (b)

Figure 35. Analysis of HWT test results for asphalt mix with 10% lignin-modified binder: (a) AASHTO method and (b) TAMU method



(a) (b)

Figure 36. Analysis of HWT test results for asphalt mix with 10% lignin-modified binder and 2.1% rejuvenator: (a) AASHTO method and (b) TAMU method

Table 10. Summary of the rutting and moisture-induced damage resistance of Asphalt mixes using AASHTO method

Properties	0% Lignin	5% Lignin	10% Lignin	10% Lignin + 2.1% Rejuvenator
Rut depth after 5,000 passes (mm)	3.69	3.63	3.00	2.79
Rut depth after 10,000 passes (mm)	5.68	5.00	4.17	4.52
Rut depth after 15,000 passes (mm)	9.65	6.59	6.53	12.67
Rut depth after 20,000 passes (mm)	13.34	8.92	9.27	-
Stripping Inflection Point (SIP)	15,750	>20,000	16,125	13,929

Table 11. Summary of the rutting and moisture-induced damage resistance of Asphalt mixes using TAMU method

Properties	0% Lignin	5% Lignin	10% Lignin	10% Lignin + 2.1% Rejuvenator
Visco-plastic Strain at Stripping Number ($\Delta\varepsilon_{LC_{SN}}^{vp}$)	$4.97*10^{-06}$	$4.35*10^{-06}$	-	$8.43*10^{-06}$
Stripping Number (LC_{SN})	4,218	7,233	4,852	1,748
Stripping Life (LC_{ST})	18,256	19,410	13,475	16,531

4.4 Characterization of Asphalt Mixes at LSU

4.4.1 Moisture-induced damage of Asphalt mixes using Modified Lottman Tests

At LSU, moisture-induced damage was evaluated using the Modified Lottman test for asphalt mixes prepared with different lignin contents. Prepared specimens were tested in triplicates for asphalt mixes with modified binder with a lignin content of 0, 5, and 10%. The level of variability in the Lottman test ranged from 1.3 to 2.6% with an average of 1.9%. Figure 37 presents the Tensile Strength Ratio (TSR) for the test combinations (0, 5, and 10% lignin). As shown in Figure 37, the mixes prepared with 5% lignin performed adequately and slightly better than the control mixture. The Louisiana recommended requirement for TSR for surface mixes is also presented in this figure.

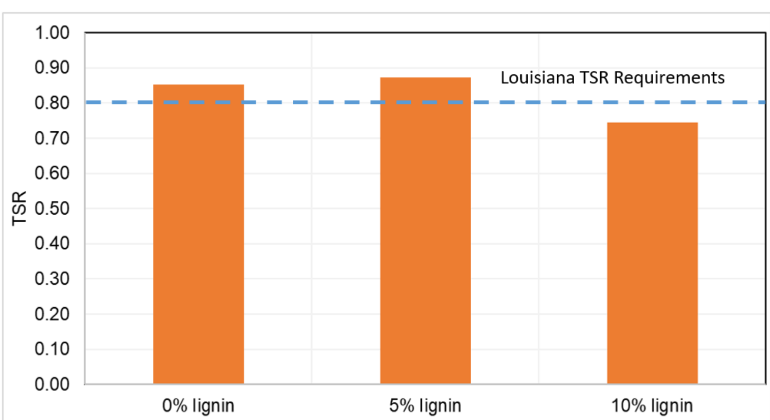


Figure 37. Tensile Strength Ratio (TSR) of Louisiana asphalt mixes

4.4.2 Cracking Resistance of Asphalt mixes using IDEAL-CT

Figure 38 presents the CT_{index} for the test combinations (0, 5, and 10% lignin). Higher CT_{index} indicates that the evaluated mixture has better cracking resistance. Different assigned letters indicate that the two groups are statistically different, with the letter A assigned to the best performer. Based on the results, the control mix (0% lignin) exhibited the highest CT_{index}, making it the best performer (Group A). This suggests that the control mixture demonstrated superior cracking resistance compared to the lignin-modified mixtures. The mix containing 10% lignin achieved a moderate CT_{index}, while the mix containing 5% lignin showed the lowest CT_{index}. However, both lignin-modified mixes fell into the same statistical category (Group B), indicating no significant difference between their cracking resistance performances. The relatively low CT_{index} values for all mixes, including the control, could be attributed to the use of unmodified asphalt binder and the RAP content in the mixes, both of which are known to reduce cracking resistance. The reduction in performance observed with the addition of lignin, particularly at 5%, suggests a potential negative effect of lignin on cracking resistance, possibly due to its interaction with the asphalt binder or its stiffening effect. These findings highlight that while lignin-modified mixes show potential in moisture resistance performance, optimization of the lignin dosage and further binder modifications may be necessary to improve cracking resistance.

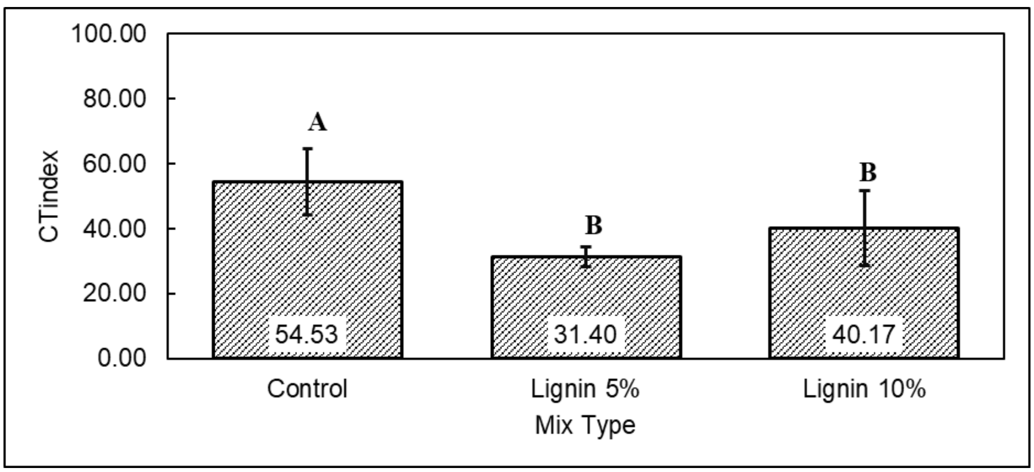


Figure 38. IDEAL-CT test results for asphalt mixes with three lignin contents at LSU

Chapter 5. Conclusions and Recommendations

The purpose of this collaborative study was to investigate the effect of lignin on the properties of asphalt binder and asphalt mixes. For this purpose, lignin was produced from rice husks using the HTC treatment process at LTU. A number of tests were used to characterize the physical and chemical properties of the rice husk derived lignin. The rice husk derived lignin was then added to a PG67-22 binder using a high shear mixing protocol. The rheological properties of the lignin-modified binders were then investigated and the effect of the addition of lignin on the properties of the binder was determined. Also, the storage stability of the lignin-modified binders was evaluated. The properties and performances of the asphalt mixes with lignin-modified binders were investigated at LSU and OU. The OU team evaluated the rutting and cracking resistance of an Oklahoma asphalt mix with lignin-modified binders. The effect of lignin on the moisture-induced damage resistance of a Louisiana asphalt mix was investigated by the LSU team. The findings of this study are summarized below.

- The HTC treatment of rice husks created a powdery substance with an increased acid insoluble lignin content and a reduced cellulose and hemicellulose content. The lignin-enriched product had a higher bulk density, indicating efficient transportability.
- The HTC treatment temperature was found to have significant impact on the production of lignin. The HTC treatment at 250℃ was more effective for lignin extraction compared to the treatment at 220℃.
- In this study, a high shear mixer with a mixing temperature of 170°C was used for preparing lignin-modified binder. From DSC thermograms, the melting point of the lignin was found to be high enough not to melt during the production of lignin-modified binder. Therefore, lignin particles are expected to be present in the modified binders.
- The storage stability test indicated that the addition of 10% lignin may produce highly unstable modified binder due to the phase separation between lignin and binder. Therefore, continuous stirring of the lignin-modified binder is recommended to reduce phase separation.
- The stability of the binder can be significantly enhanced by reducing the lignin particle size along with SBS modification. Subsequent investigations into the optimum dosage of lignin in conjunction with a compatible elastomer may yield significantly enhanced performance of asphalt binder.
- The modification of asphalt binder with lignin exhibited an increase in the rutting resistance in comparison to the neat binder. Approximately 2°C grade bumping at high-temperature continuous PG was observed with the addition of 10% lignin.
- From MSCR test, the lignin modification had lowered the J_{nr} value at both stress levels compared to the neat binder indicating better resistance to rutting with the addition of lignin to neat binder. Also, slight improvement in %Recovery was observed for the lignin-modified binders.
- The low-temperature properties of the asphalt binder were found to be negatively impacted by the addition of lignin as it caused an increase in stiffness and reduction in m-value at low temperatures. The addition of 10% lignin was found to increase the low-temperature continuous grade by 3.4°C.
- Satisfactory moisture-induced damage resistance was observed in asphalt mixes with lignin-modified binders. The Louisiana asphalt mixes prepared with 5% lignin exhibited slightly better moisture-induced damage resistance than that of control mix.
- The HWT tests indicated that the mixes with lignin-modified binders satisfied the specification requirements for rutting resistance for Oklahoma mixes. Also, asphalt

mixes with 5% and 10% lignin-modified binders exhibited stripping inflection point at wheel passes higher than 15,000 indicating good resistance to moisture-induced damage.

- The ITS value was found to increase with an increase in the lignin content. An increase in stiffness with the addition of lignin was responsible for the increase in ITS value.
- The failure energies of asphalt mix specimens were observed to increase with an increase in lignin content. The asphalt mix with 5% lignin showed the highest failure energy among other mixes. Also, the post peak slope of the asphalt mix was found to increase significantly with the use of lignin-modified binders. The results indicate that the asphalt mixes became stiff and brittle with the use of lignin-modified binder.
- Cracking resistance of the asphalt mixes with lignin-modified binders was found to reduce significantly with the addition of lignin. As the lignin-modified binders exhibited a $G^*. \sin \delta$ value greater than 5,000 kPa, it was expected that the asphalt mixes with lignin-modified binders will exhibit poor resistance to cracking. None of the asphalt mixes with lignin-modified binders satisfied the Oklahoma DOT specification for CT_{index}. The addition of rejuvenator was found not to be helpful to improve cracking resistance.
- The findings indicated that the modification of binder with lignin has potential to improve the properties and performances of asphalt binder and asphalt mix, with the exception of cracking resistance. Therefore, a partial replacement of fossil fuel-based binder with lignin is feasible with measures to improve cracking resistance.

The following recommendations were drawn from this study:

- As found in previous research conducted by King (2008), lignin in asphalt binder act as an asphalt extender. As an asphalt extender, minimum binder contents may warrant reduction if other performance tests indicate good performance.
- While the changes in binder and mix performance were minimal, the lignin used in this work affected the high-temperature properties slightly more than low-temperature properties. As such, fatigue performance would likely be the more predominate governing factor in the asphalt mix design process.
- As typically done with other additives like ground tire rubber, the mix design and field mixing methods can fall into 3 categories. Category-1: design using wet-process. This means adding lignin to the binder. Category-2: use dry-process and add the lignin to the aggregates. Category-3: a hybrid process where it is designed in the laboratory using the wet-process but method (2) is used for field production of asphalt mix.
- If the wet-process is used for field construction, it is recommended that the blend of lignin and binder be pumped into the mix from the transport rather than the plant’s asphalt binder storage tank. Agitation may be required to prevent separation of lignin from the binder during storage.
- Only one type of binder was investigated in this study, and future work is needed to incorporate other types of binder and varying lignin contents. Also, the use of lignin from other unused secondary agricultural and forestry residues is recommended.

Chapter 6. Implementation of Project Outputs

This project used a renewable resource like rice husk derived lignin as a paving material, and generated knowledge and guidelines on using lignin in asphalt mixes. The findings of this study will be of tremendous help to the stakeholders including transportation agencies and manufacturers. This solution is expected to significantly reduce the construction costs.

Further work on the asphalt binder modified by lignin obtained from HTC treatment process will be required before commercial implementation can be achieved. Also, bulk production of lignin will need to be developed for field construction. For the dry or hybrid field construction methods, use of a dry feeder, such as a Hi-Tech feeder can add lignin to the top of a mix drum at the asphalt plant. However, careful metering of the lignin similar to what is done with the dry process of ground tire rubber will be required.

While evaluation of test sections in the field is warranted, logistics need to be refined before large scale construction should begin. A small test section could be constructed at an asphalt plant's yard, University road, private parking lot, or other sacrificial/temporary section. Phase 2 of this research could demonstrate the feasibility of constructing a small test section and performance monitoring. Phase 3 would be a test section at an accelerated test track facility. Phase 4 would be a small project, such as constructing a county road. Phase 5 would be constructing pilot test sections on state or county highways.

Chapter 7. Technology Transfer and Community Engagement and Participation (CEP) Activities

A poster was presented at the 2024 Oklahoma Summer Transportation Symposium, held on July 30, 2024, in Oklahoma City, OK. Another poster was presented on October 15, 2024 at the 2024 Oklahoma Transportation Research Day in Edmond, OK.

A webinar to present research results to industry members is scheduled for April 16, 2025. Southern Plains Transportation Center (SPTC) will host the webinar.

Chapter 8. Invention Disclosures and Patents, Publications, Presentations, Reports, Project Website, and Social Media Listings

A publication is being written for submission to Construction and Building Materials to disseminate the research results.

A webinar to present research results to industry members is scheduled for April 16, 2025.

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