SUSTAINABLE MODIFICATION OF BITUMEN AND ASPHALT MIXES WITH KRAFT LIGNIN

by

Ali REZAZAD GOHARI

MANUSCRIPT-BASED THESIS PRESENTED TO ÉCOLE DE TECHNOLOGIE SUPÉRIEURE IN PARTIAL FULFILLMENT FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
PH.D.

MONTREAL, JUNE 30, 2025

ÉCOLE DE TECHNOLOGIE SUPÉRIEURE
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FOREWORD

The journey of this PhD research has been one of exploration, innovation, and dedication. Focused on advancing the sustainability and performance of asphalt technologies, this thesis embodies a commitment to addressing pressing environmental and engineering challenges in the field of pavement materials. Through a comprehensive investigation into Kraft lignin and its synergistic effects with Sasobit, this research explores novel approaches to modifying bitumen and asphalt mixtures.

This work reflects not only the culmination of years of rigorous study but also the collaborative efforts and the invaluable guidance of supervisors, advisors, technicians, colleagues, and collaborators. It highlights the significance of integrating sustainable materials into asphalt production processes and aims to contribute to the growing body of knowledge that seeks to harmonize infrastructure development with environmental stewardship.

The manuscript-based structure of this thesis encompasses three published and submitted articles, each representing a pivotal phase of the research. These phases collectively cover the blending conditions and chemo-thermal properties of lignin-modified bitumen, the synergistic interactions of lignin and Sasobit, and the application of these additives in asphalt mixtures. I hope this thesis serves as a meaningful contribution to the scientific community and inspires further advancements in the field of sustainable asphalt technologies. It is with great gratitude and humility that I present this work as a testament to the shared pursuit of knowledge and innovation.

ACKNOWLEDGMENTS

The PhD journey is a long, challenging path, one that requires patience, commitment, and perseverance. For me, this journey was marked by the isolation and uncertainty of the COVID-19 pandemic and the emotional weight of being far from my family and beloved homeland, Iran. Despite these challenges, life brought profound joy—I met and married my beloved wife, and together, we welcomed our son, Nik, whose presence has been a source of motivation and happiness.

I am deeply grateful to my family for their unwavering support. My father, Mohammadreza, has always guided me with wisdom and belief in my abilities. My mother, Ozra, has been my sanctuary with her unconditional love and encouragement. My wife, Roshanak, has stood by me with extraordinary patience and support, especially during long nights of study and research. My sisters, Faezeh and Fereshteh, have been a source of kindness and encouragement throughout this journey.

I extend my heartfelt gratitude to my supervisors, Mr. Alan Carter and Mr. Jean-Pascal Bilodeau, for their exceptional guidance and support. Mr. Carter’s professionalism and mentorship have been invaluable, while Mr. Bilodeau’s kindness and guidance have shaped my academic growth. I am also grateful to Mr. Sébastien Lamothe, whose expertise and dedication significantly impacted my research, as well as Mr. Ahmad Mansourian, my master’s supervisor, for his encouragement and technical support.

I sincerely appreciate the support of Sylvain Bibeau, Francis Bilodeau, Victor Brial, and Radu Romanica in my experimental work. I also thank Mr. Philippe Bocher, president of the jury and the jury members, including Mr. Daniel Perraton and Mrs. Cassie Castorena, for their time and valuable feedback. Special thanks to Veronique Szabo (Suncor), FPInnovations for providing lignin, and Daniel Liao (University of Waterloo) for ESEM tests. Lastly, I am grateful to the LCMB group at ÉTS and my office friends for making this journey more enjoyable.

MODIFICATION DURABLE DU BITUME ET DES ENROBES AVEC LA KRAFT LIGNIN

Ali REZAZAD GOHARI

RÉSUMÉ

Les revêtements en asphalte sont essentiels aux infrastructures modernes, mais les méthodes conventionnelles peinent souvent à répondre aux exigences croissantes de durabilité tout en maintenant une performance fiable. Cette recherche doctorale explore le potentiel des additifs durables, notamment la Kraft lignin. La recherche s'est déroulée en trois phases, en se concentrant sur la Kraft lignin. Lors de la première phase, les propriétés clés de la Kraft lignin, telles que la distribution granulométrique et les caractéristiques chimio-thermiques, ont été étudiées. Par la suite, la Kraft lignin a été incorporée au bitume en utilisant deux protocoles de mélange afin d'évaluer les effets des conditions de mélange et de la teneur en lignine. Divers tests (BRV, DSR, FTIR, ESEM, TGA, DSC) ont été réalisés. Les résultats ont démontré des influences significatives de la teneur en Kraft lignin et des conditions de mélange sur la viscosité, le comportement viscoélastique et la stabilité thermique, tandis que les analyses FTIR ont confirmé l'absence de réaction chimique avec le bitume. La deuxième phase s'est concentrée sur l'atténuation de l'augmentation de la viscosité observée dans le bitume modifié par la Kraft lignin en utilisant le Sasobit®. Les effets synergiques de la Kraft lignin et du Sasobit ont été étudiés à l'aide de tests FTIR, TGA, BRV, DSR, MSCR et BBR. Les résultats ont montré que le Sasobit réduisait efficacement la viscosité du bitume modifié par la Kraft lignin, améliorait la stabilité thermique et renforçait la performance à haute température, bien que la performance à basse température ait été légèrement compromise. La troisième phase a élargi la recherche aux Enrobé, en évaluant les effets combinés de la Kraft lignin et du Sasobit dans des enrobés à chaud (HMA) et tièdes (WMA). Les propriétés volumétriques et massiques, la compactabilité et les températures de mise en œuvre ont été évaluées à l'aide du PCG. Bien que la Kraft lignin ait entraîné une augmentation de la viscosité du liant et des vides d'air, ce qui a conduit à des températures de mise en œuvre plus élevées et à une compactabilité réduite, le Sasobit a efficacement compensé ces effets. De plus, la Kraft lignin a montré un rôle double, à la fois en tant que substitut partiel du liant et en tant que filler. La combinaison de 20 % de Kraft lignin et de 3 % de Sasobit a démontré un potentiel significatif pour promouvoir une production d'asphalte plus durable.

Mots-clés : Additifs durables, Kraft lignin, enrobés tièdes, modification du bitume, propriétés des enrobés

SUSTAINABLE MODIFICATION OF BITUMEN AND ASPHALT MIXES WITH KRAFT LIGNIN

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ABSTRACT

Asphalt pavements are vital to modern infrastructure, but conventional methods often struggle to address growing sustainability demands while maintaining reliable performance. This PhD research aims to investigate the potential of sustainable additives, specifically Kraft lignin, to address these challenges. The research began with a preliminary investigation into Aluminosilicate, as a warm mix asphalt modifier, which lacked the necessary properties for an effective additive, prompting a shift toward Kraft lignin. The study was initiated by evaluating different lignin types and then continued in three phases, focusing on Kraft lignin. In the first phase, key properties of Kraft lignin, including particle size distribution and chemo-thermal characteristics, were investigated. Subsequently, Kraft lignin was incorporated into bitumen using two mixing protocols: high-shear mixer and mechanical mixer, to evaluate the effects of Kraft lignin and blending conditions. A comprehensive series of tests, including BRV, DSR, FTIR, ESEM, TGA, and DSC, were conducted. The results demonstrated significant influences of Kraft lignin content and blending conditions on viscosity, viscoelastic behavior, and thermal stability, while FTIR confirmed no chemical reaction with bitumen. The second phase focused on mitigating the increased viscosity observed in lignin-modified bitumen using Sasobit®. The synergistic effects of Kraft lignin and Sasobit were investigated using FTIR, TGA, BRV, DSR, MSCR, and BBR tests on bitumen. Results demonstrated that Sasobit effectively reduced the viscosity of lignin-modified bitumen, enhanced thermal stability, and improved high-temperature performance, although low-temperature performance was slightly compromised. The third phase extended the research to asphalt mixes, evaluating the combined effects of Kraft lignin and Sasobit on hot and warm mix asphalt. Four Mixes with 20 % Kraft lignin and 3 % Sasobit, were produced. Volumetric and mass properties, compactability, and construction temperatures were evaluated using the SGC. While Kraft lignin increased binder viscosity and air voids, leading to higher construction temperatures and reduced compactability, Sasobit effectively counteracted these effects. Additionally, Kraft lignin exhibited a dual role, as both a binder replacement and a filler. The combination of 20 % Kraft lignin and 3 % Sasobit demonstrated significant potential for advancing sustainable asphalt production.

Keywords: Sustainable additives, Kraft lignin, Warm Mix Asphalt (WMA), Bitumen modification, Asphalt mix properties

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LIST OF ABREVIATIONS AND ACRONYMS

20L	Modified Bitumen with 20 % Kraft lignin
20L3S	Modified Bitumen with 20 % Kraft lignin and 3 % Sasobit
3S	Modified Bitumen with 3 % Sasobit
AASHTO	American Association of State Highway and Transportation Officials
ASTM	American Society for Testing and Materials
ATR-FTIR	Attenuated Total Reflectance- Fourier Transform Infrared Spectroscopy
BBR	Bending Beam Rheometer
BCMWMA	Buton rock asphalt Composite Modified Warm Mix Asphalt
BRA	Buton Rock Asphalt
BRV	Brookfield Rotational Viscometer
CBM	Construction and Building Materials
CMA	Cold Mix Asphalt
CRM	Crumb Rubber Modifier
DLS	Dynamic Light Scattering
DSC	Differential Scanning Calorimetry
DSR	Dynamic Shear Rheometer
DTG	Derivatives Thermogravimetric
EQ	Equi-viscous
ESEM	Environmental Scanning Electron Microscopy

ESG	Enrobé Semi-Grenu
EVA	Ethylene-Vinyl Acetate
FDT	Final Decomposition Temperature
FR	Final Residue
FTIR	Fourier Transform Infrared Spectroscopy
FWHM	Full Width at Half Maximum
GHG	Greenhouse Gas
H-grade	High-temperature Grade
HMA	Hot Mix Asphalt
HMA-20L	Hot Mix Asphalt with 20 % Kraft lignin
HMA-REF	Reference Hot Mix Asphalt
HSM	High-Shear Mixing
HTSWA	Acid-form Hinton lignin
HTSWB	Base-form Hinton lignin
HWMA	Half Warm Mix Asphalt
IDT	Initial Decomposition Temperature
KSWA	Acid-form Kruger lignin
KSWB	Base-form Kruger lignin
L	Kraft lignin
LC	Laboratoire des chaussées
LCA	Life Cycle Assessment
LCPC	Laboratoire Central des Ponts et Chaussées

LDPE	Low-Density Polyethylene
L-grade	Low-temperature Grade
LLDPE	Linear Low-Density Polyethylene
LVE	Linear Viscoelastic
M	Mixing
MM	Mechanical Mixing
MRDT	Maximum Rate of Decomposition Temperature
MSCR	Multiple Stress Creep Recovery
MTMD	Ministère des Transports et de la Mobilité Durable
MTQ	Quebec's Ministry of Transportation
NMAS	Nominal Maximum Aggregate Size
NMX	Nemaska Lithium Inc.
OGFC	Open-Graded Friction Course
PAV	Pressure Aging Vessel
PG	Performance Grading
PmB	Polymer-modified Bitumen
PSD	Particle Size Distribution
RAP	Reclaimed Asphalt Pavement
RAS	Reclaimed Asphalt Shingles
REF	Reference
RMPD	Road Materials and Pavement Design
RTFOT	Rolling Thin Film Oven test

S	Standard
S	Sasobit
SBRMA	Styrene-Butadiene Rubber-Modified Asphalt
SBS	Styrene-Butadiene-Styrene
SE	Secondary Electron
SEM	Scanning Electron Microscopy
SGC	Superpave Gyratory Compactor
SHRP	Strategic Highway Research Program
SMA	Stone Mastic Asphalt
Superpave	Superior Performing Asphalt Pavement
TBHWA	Acid-form Thunder Bay lignin
TBHWB	Base-form Thunder Bay lignin
TGA	Thermogravimetric Analysis
TL-DSC	Temperature Linear-Differential Scanning Calorimetry
TM-DSC	Temperature Modulation-Differential Scanning Calorimetry
VB	Virgin Bitumen
VFA	Voids Filled with Asphalt
VMA	Voids in Mineral Aggregate
WMA	Warm Mix Asphalt
WMA-20L3S	Warm Mix Asphalt with 20 % Kraft lignin and 3 % Sasobit
WMA-3S	Warm Mix Asphalt with 3 % Sasobit

LIST OF SYMBOLS

G^*	complex shear modulus
$\lvert G^* \rvert$	norm of the complex shear modulus
a.u.	arbitrary units
b	width of the beam
CH_4	methane
CO_2	carbon dioxide
CO_2e	carbon dioxide equivalent
–C–O–C–	ether bonds
D_1	temperature at which 1 % of the sample decompose
D_{10}	temperature at which 10 % of the sample decompose
D10	particle diameter at which 10% of the sample's mass is smaller
D_5	temperature at which 5 % of the sample decompose
D_{50}	temperature at which 50 % of the sample decompose
D50	particle diameter at which 50% of the sample's mass is smaller (median particle size)
D90	particle diameter at which 90% of the sample's mass is smaller
E	extremely heavy traffic
G_b	specific gravity of the binder
G_{mb}	bulk density
G_{mm}	theoretical maximum specific gravity
h	thickness of the beam

H	heavy traffic
H-grade	high temperature grade
J_{nr}	non-recoverable creep compliance
$J_{nr0.1}$	non-recoverable creep compliance at 0.1 kPa
$J_{nr3.2}$	non-recoverable creep compliance at 3.2 kPa
J_{nrdiff}	difference in non-recoverable creep compliance between the two stress levels
L	distance between the supports
L-grade	low temperature grade
m(60)	creep relaxation
M_a	mass of air
M_{agg}	mass of aggregate
M_b	total mass of binder
M_{ba}	mass of absorbed binder
M_{be}	mass of effective binder
N_2	nitrogen
N_2O	nitrous oxide
N_{design}	gyrations for expected service compaction
N_{final}	gyrations for maximum traffic loading
$N_{initial}$	gyrations for construction compaction
–OH	hydroxyl
P	load applied

P_b	binder content
P_{ba}	absorbed binder by the aggregates
pH	potential of hydrogen
$R_{3.2}$	average recovery of strain
S	standard traffic
S(60)	creep stiffness modulus
S(t)	stiffness at time t
$T_{compaction}$	compaction temperature
T_g	glass transition temperature
T_{high}	high temperature
T_{low}	low temperature
T_{mixing}	mixing temperature
T_T	testing temperature
V	very heavy traffic
V_a	air voids
V_{ba}	volume of absorbed binder
V_{be}	volume of effective binder
V_{gb}	aggregate volume by bulk specific gravity
δ	phase angle
$\delta(t)$	deflection at time t
$\Delta T_{compaction}$	compaction temperature changes
ΔT_{mixing}	mixing temperature changes

INTRODUCTION

Asphalt pavements are essential components of modern infrastructure, relying on bitumen as a durable binder. However, traditional asphalt binders exhibit limitations in their thermal and rheological properties, which can negatively impact performance and sustainability. Likewise, asphalt mixtures face challenges related to workability, compaction, durability, and mechanical performance, particularly under varying climatic and loading conditions. These limitations necessitate the development of modified binders and asphalt mixtures that offer improved performance while reducing environmental impact. Modifying bitumen and asphalt mix with bio-based additives has become crucial to enhance these properties and reduce the environmental footprint of asphalt production.

The asphalt industry is increasingly adopting sustainable practices to mitigate the environmental impact of traditional production methods, which rely heavily on high-temperature processes. These methods consume significant energy and deplete natural resources. This study evaluates Kraft lignin, a renewable biopolymer and by-product of the paper industry for bitumen and asphalt mixture modification. By utilizing and valorizing Kraft lignin as a sustainable material and analyzing the combined effects of these additives on bitumen and asphalt mix properties, this research seeks to advance both sustainability and performance in asphalt applications.

Traditional asphalt production depends on oil-based bitumen and high-temperature processes, consuming significant energy and emitting substantial greenhouse gases. These practices contribute to environmental concerns and highlight the urgent need for sustainable alternatives. Furthermore, conventional bitumen and asphalt mixes often struggle to meet the evolving performance requirements of modern infrastructure. Key challenges include ensuring the effective incorporation of additives into bitumen and asphalt mix, evaluating their performance under varying conditions, and maintaining compatibility with sustainable practices. Addressing these limitations demands innovative solutions that enhance the performance of bitumen and asphalt mixtures while aligning with sustainability goals by utilizing bio-based by-products from other industries, such as lignin, and reducing energy consumption and environmental impact.

This research investigates the effects of Kraft lignin on bitumen and asphalt mix properties. Objectives include:

- Investigating different lignin types by analyzing their particle size distribution (PSD) and dispersion behavior.
- Investigating some critical properties of Kraft lignin and optimizing its blending conditions with bitumen to produce lignin-modified bitumen.
- Evaluating the combined effects of Kraft lignin and Sasobit on the rheological and chemo-thermal properties of modified bitumen.
- Assessing the impact of Kraft lignin and Sasobit on the basic properties of Hot Mix Asphalt (HMA) and Warm Mix Asphalt (WMA), including volumetric and mass properties, compactability, and construction temperatures, to evaluate their feasibility for practical applications.

Modified bitumen samples were prepared with varying Kraft lignin and Sasobit concentrations. The samples were tested using:

- **Properties of Kraft Lignin:** Analysis of particle size distribution (PSD) and thermo-chemical properties.
- **Rheological Tests:** Brookfield Rotational Viscometer (BRV), Dynamic Shear Rheometer (DSR), Multiple Stress Creep Recovery (MSCR), and Bending Beam Rheometer (BBR).
- **Chemical, Thermal, and Morphological Analysis:** Fourier Transform Infrared Spectroscopy (FTIR), Environmental Scanning Electron Microscopy (ESEM), Thermogravimetric Analysis (TGA), and Differential Scanning Calorimetry (DSC).
- **Compaction and Volumetric Properties:** Mix Design and Superpave Gyratory Compactor (SGC).

These tests provided insights into the additives' impact on performance and sustainability.

This thesis explores sustainable bitumen and asphalt mix modification using Kraft lignin and Sasobit, presenting findings across seven chapters:

- **Chapter 1: Literature Review** — A comprehensive overview of sustainable asphalt additives, including bio-based materials such as lignin and WMA technologies.
- **Chapter 2: Research Objective and Experimental Plan** — outlines the global approach to the experimental program, detailing the phases of the research, the methodologies employed, and the main objectives of the thesis.
- **Chapter 3: A Preliminary Evaluation of Aluminosilicate as an Additive in Warm Mix Asphalt: Challenges and Results** — Presents an initial investigation into the potential use of Aluminosilicate as an additive in WMA, highlighting key challenges and limitations observed during the study.
- **Chapter 4: Particle Size Distribution of Different Types of Lignin**— Investigates the particle size distribution of various types of lignin, providing essential insights into their physical characteristics.
- **Chapter 5: Laboratory Study on Influence of Blending Conditions on Chemo-Thermal Characteristics of Lignin-Modified Bitumen** — Published in journal of Applied Sciences, this chapter evaluates Kraft lignin properties and blending protocols of lignin-modified bitumen.
- **Chapter 6: Laboratory Study on Synergistic Effects of Sasobit® on Rheological and Chemo-Thermal Properties of Lignin-Modified Bitumen** — Published in International Journal of Road Materials and Pavement Design (RMPD), it explores the combined impacts of Kraft lignin and Sasobit in bitumen.
- **Chapter 7: Laboratory Study on the Effects of Kraft Lignin and Sasobit® on Construction Temperatures, Compactability and Physical Properties of Hot and Warm Mix Asphalt** — Submitted to Construction and Building Materials (CBM), this chapter focuses on volumetric and mass properties, compactability and construction temperatures in HMA and WMA.
- **Chapter 8: Comprehensive Synthesis of Experimental Findings and General Discussion** — Integrates key findings from all experimental phases, discussing the

different lignin types, Kraft lignin effect, blending conditions, and the synergy between Sasobit and Kraft lignin on bitumen and asphalt mix properties.

- **Conclusion** — Summarizes key findings.
- **Recommendations** — Contributions and proposes future research directions.

CHAPTER 1

LITERATURE REVIEW

1.1 The Asphalt Industry

The asphalt industry plays a crucial role in modern infrastructure by producing and supplying materials essential for constructing and maintaining roads and highways. Asphalt mixtures consist of aggregates (94–96 %) and asphalt binder (4–6 %), derived from the fractional distillation of crude oil (Milad et al., 2022). Notably, approximately 90 % of the world's paved roads are constructed using asphalt mixtures (Zapata & Gambatese, 2005). Global demand for asphalt is rising due to expanding infrastructure and urbanization, particularly in emerging economies. At asphalt plants, aggregates are dried and heated to ensure proper bonding with the asphalt binder, creating a homogeneous mixture. The asphalt industry's dependence on fossil fuels and energy-intensive high-temperature processes significantly contributes to greenhouse gas emissions and the depletion of natural resources such as petroleum and aggregates (Thives & Ghisi, 2017). Addressing these environmental challenges necessitates the development of sustainable practices that balance infrastructure development with environmental responsibility.

1.2 Bitumen

Bitumen is the primary binder used in asphalt pavements. Its critical role is providing structural integrity and durability to asphalt mixtures, ensuring long-lasting and resilient pavements. Despite constituting a small proportion of the asphalt mixture by weight, bitumen accounts for a significant portion of the material costs due to its essential role. Asphalt pavements are widely preferred for their high performance, ease of maintenance, and ability to deliver smooth and comfortable driving conditions. The quality of bitumen is essential for the durability of asphalt mixtures. It must consider specific climate and traffic conditions to optimize performance (Roberts, Kandhal, Brown, Lee, & Kennedy, 1996). As a derivative of crude oil, bitumen is inherently linked to sustainability challenges, a resource that cannot be replaced. The properties of bitumen are shaped not only by the type of crude oil used but also by the refining techniques employed during production. These factors require careful consideration to balance quality with environmental impact (Hunter, Self, Read, & Hobson, 2015).

1.2.1 Chemical Structure and Composition

Bitumen is a sophisticated and complex blend of hydrocarbons, combined with small amounts of elements such as oxygen, sulfur, and nitrogen (Hunter et al., 2015; Romberg, Nesmith, & Traxler, 1959). To facilitate a deeper understanding of bitumen's structure, researchers commonly employ SARA fractionation, a method that categorizes bitumen into four polarity-based fractions: Saturates (S), Aromatics (A), Resins (R), and Asphaltenes (A) (Beitchman, 1959; Corbett, 1969; Such, Brule, & Baluja-Santos, 1979). This classification is not molecularly precise but rather reflects a polarity gradient. Among these, asphaltenes, the most polar fraction, form nanoaggregates and clusters, significantly impacting bitumen's physical and mechanical properties. Conversely, the less polar maltenes—comprising saturates, aromatics, and resins—function as a solvent for the asphaltenes. The dynamic interaction between asphaltenes and maltenes, particularly the aggregation and dispersion of asphaltenes, plays a critical role in determining bitumen's viscoelastic behavior (Sakib & Bhasin, 2019).

Temperature is a key factor in bitumen's viscoelastic properties, dictating its response to mechanical stress (Pipintakos, Sreeram, Mirwald, & Bhasin, 2024). At elevated temperatures, bitumen exhibits fluid-like viscous behavior, making it prone to rutting under heavy loads. At lower temperatures, it behaves as a brittle elastic solid, increasing its susceptibility to cracking (Little, Allen, & Bhasin, 2018).

1.2.2 Grading Systems

Bitumen grading traditionally relies on physical properties such as penetration depth and softening point, particularly in Europe. However, these methods often fail to capture the complexities of modern binder formulations, especially those modified with additives. To address this, there is a growing shift toward performance-based grading systems, especially in the United States, which link binder properties to expected performance across varying climates and traffic conditions. Performance Grading (PG), for instance, evaluates binders under specific high- and low-temperature ranges, offering insights into their resistance to rutting, fatigue, and thermal cracking. The selection of an appropriate grade is critical to ensuring durability, as the bitumen must meet the specific demands of varying climate and traffic conditions (Wess, Olsen, & Sweeney, 2004).

1.3 Asphalt Mixes

The performance and sustainability of asphalt pavements depend on the type of mix used, with Hot Mix Asphalt (HMA), Warm Mix Asphalt (WMA), and Cold Mix Asphalt (CMA) being the most common (Figure 1.1). Each type has distinct production processes, properties, and applications, designed to meet specific climate, traffic, and environmental requirements (Lavin, 2003).

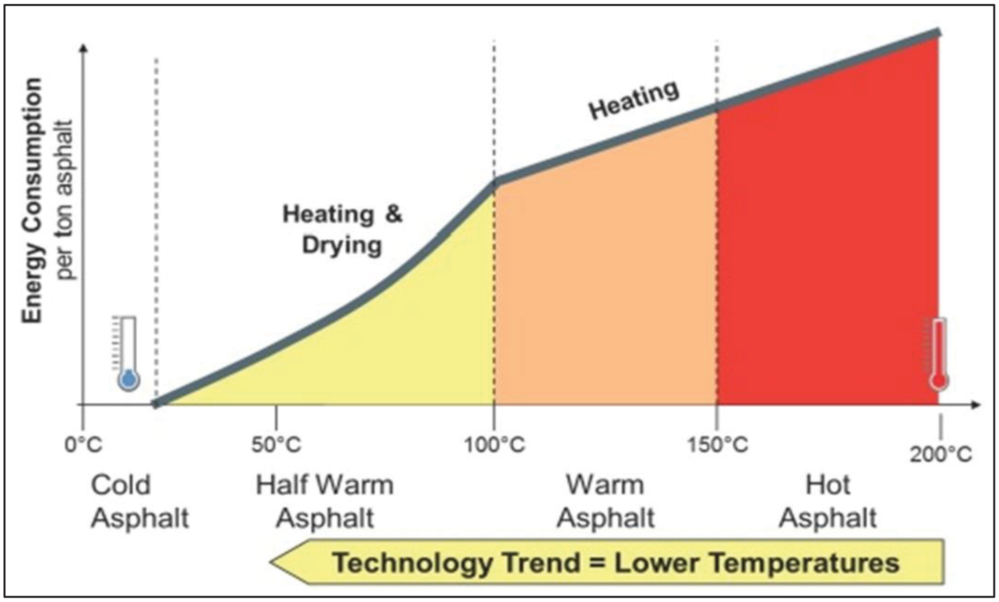


Figure 1.1 Comparison of asphalt mix types based on production temperatures and energy consumption
Taken from Zaumanis (2014)

1.3.1 Hot Mix Asphalt (HMA)

HMA is produced and applied at high temperatures, typically ranging between 150 and 200 °C. These elevated temperatures ensure that asphalt cement maintains the proper viscosity for effective mixing and compaction. HMA is manufactured in two main types of plants: batch plants, which allow for precise control of individual batches, and drum plants, which offer continuous production for improved efficiency. Proper storage and handling of HMA are essential to prevent the segregation of aggregates and ensure homogeneity. However, the high temperatures required for production and application result in significant energy consumption and greenhouse gas emissions, prompting the development of alternative solutions (Roberts et al., 1996).

1.3.2 Warm Mix Asphalt (WMA)

WMA technologies provide a more sustainable alternative to HMA by lowering production and application temperatures by 10 to 45 °C. This reduction is achieved through various methods, including organic additives like Sasobit, which reduce the viscosity of the asphalt binder, and foaming techniques that enhance coating and compaction at reduced temperatures. WMA offers several environmental and operational advantages. Reduced production temperatures decrease energy consumption and greenhouse gas emissions, contributing to sustainability goals (Figure 1.2). Additionally, lower temperatures improve working conditions by minimizing exposure to fumes and heat. WMA enhances compaction, extends hauling distances by slowing the cooling process, and facilitates higher incorporation of Reclaimed Asphalt Pavement (RAP), further reducing the need for virgin materials. Its ability to perform comparably to HMA under diverse conditions has made WMA a viable option for regions prioritizing sustainability and resource efficiency (Prowell, Hurley, & Frank, 2011).

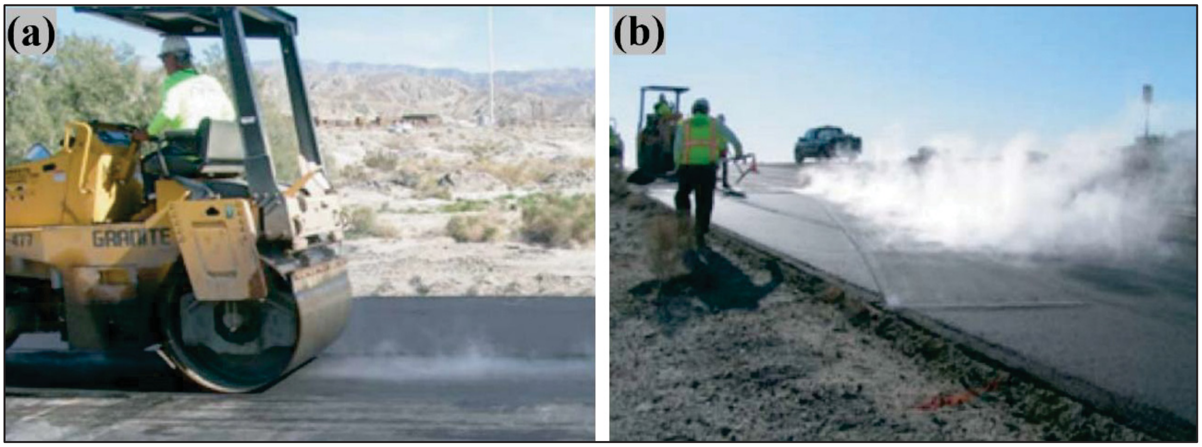


Figure 1.2 Steams emitted from WMA (a) and HMA (b) during compaction
Taken from Wielinski et al. (2009)

1.3.3 Cold Mix Asphalt (CMA)

CMA is produced by mixing unheated aggregates with emulsified or cutback bitumen, eliminating the need for heating. This makes CMA a cost-effective and energy-efficient option for minor construction and repair works. However, CMA has limitations, including lower early-life strength, higher air voids, and increased moisture susceptibility compared to HMA and WMA. The prolonged curing time, required for water evaporation, restricts CMA's use in high-traffic or time-sensitive projects. Despite these constraints, CMA remains a practical solution for low-traffic applications (Jain & Singh, 2021).

Following the discussion of the types of asphalt mixes, understanding the durability and deformation resistance of these mixes is essential to ensuring their long-term performance under diverse traffic and environmental conditions. Durability refers to the ability of the mix to maintain its structural integrity over time, resisting issues such as aging and cracking. Equally important is the mix's resistance to deformation, particularly rutting, which is critical for maintaining a smooth and safe pavement surface. Several factors, including aggregate angularity, optimal volumetric properties, asphalt binder content, binder grade, and resistance to aging and moisture damage influence these performance properties. Moreover, incorporating appropriate additives and employing precise mix designs can significantly enhance these properties (Hunter, 1994).

The selection of an asphalt mix also depends on specific requirements such as traffic levels, climate conditions, layer thickness, and the intended performance goals. For instance, dense-graded mixes offer versatility and are suitable for a wide range of traffic conditions. Gap-graded mixes, like Stone Mastic Asphalt (SMA), perform well in providing superior durability and rutting resistance but require the use of high-quality materials. Open-graded mixes, such as the Open-Graded Friction Course (OGFC), are designed for effective drainage, mitigating hydroplaning risks and efficiently managing water within the pavement structure. By customizing the mix design to meet these functional and operational needs, the performance and sustainability of asphalt pavements can be optimized (Thom, 2024).

1.4 Sustainability in Asphalt

1.4.1 Sustainable Practices in Asphalt Production

Sustainability in asphalt production necessitates a multifaceted approach, combining innovative technologies, bio-based materials, and recycling strategies to mitigate environmental impact (Al-Jumaili, 2018; Enieb, Al-Jumaili, Al-Jameel, & Eltwati, 2021; Hegab, Khanna, Monib, & Salem, 2023; Mantalovas & Di Mino, 2020). Efforts to reduce the environmental impact of asphalt production have led to the development of innovative practices and technologies. WMA technologies, for example, reduce production temperatures by 25 to 50 %, significantly lowering energy consumption and greenhouse gas emissions (Tutu & Tuffour, 2016). Another key approach is incorporating bio-based additives, aligning with circular economy principles, reducing dependency on non-renewable resources while improving the environmental profile of asphalt (Fini, 2016). Figure 1.3 illustrates the core aspects of sustainability in asphalt production, which include economy, environment, and engineering. The asphalt industry is increasingly adopting circular economy strategies, emphasizing the reuse and recycling of materials to reduce waste and resource consumption. Materials like RAP, Reclaimed Asphalt Shingles (RAS), and Crumb Rubber Modifier (CRM) have gained attention due to their environmental benefits (Pouranian & Shishehbor, 2019).

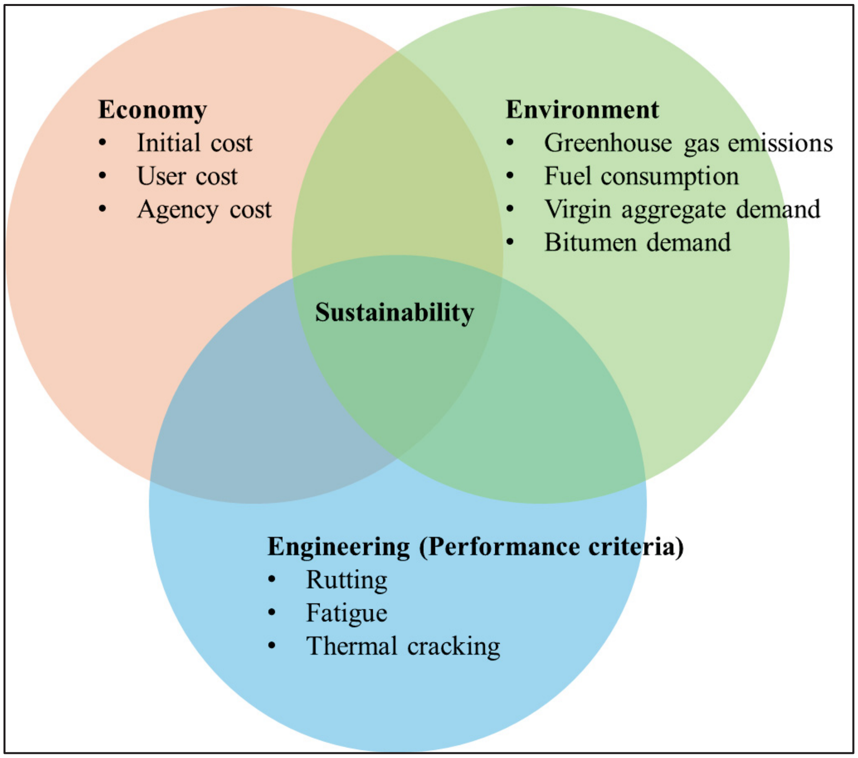


Figure 1.3 Core aspects of sustainability in asphalt production: economy, environment, and engineering

Taken from Pouranian & Shishehbor (2019)

1.5 Additives in Bitumen Modification

While sustainable practices in asphalt production focus on reducing environmental impacts through innovative technologies and recycling strategies, the use of additives provides another effective approach to enhance both the performance and sustainability of asphalt mixtures. Additives play a vital role in modifying bitumen properties to address the challenges caused by varying environmental conditions and increasing traffic demands. This section discusses the diverse range of additives used in bitumen modification, their mechanisms, and their influence on the functional and environmental characteristics of asphalt pavements.

The modification of bitumen with additives has become a fundamental practice in asphalt production to address the limitations of conventional bitumen and improve performance properties such as elasticity, resistance to aging, rutting and cracking (You, Dai, & Xiao, 2018).

Various types of additives, each with distinct properties and mechanisms, play a crucial role in enhancing bitumen's functionality under varying conditions. Polymers, such as styrene-butadiene-styrene (SBS), ethylene-vinyl acetate (EVA), and Low-Density Polyethylene (LDPE), are commonly used to improve the flexibility and strength of bitumen (Figure 1.4). These additives form a network within the bitumen matrix, enhancing its resistance to deformation and increasing elasticity (Behnood & Gharehveran, 2019; Diab, Enieb, & Singh, 2019; Polacco, Filippi, Merusi, & Stastna, 2015; Jiqing Zhu, Birgisson, & Kringos, 2014).

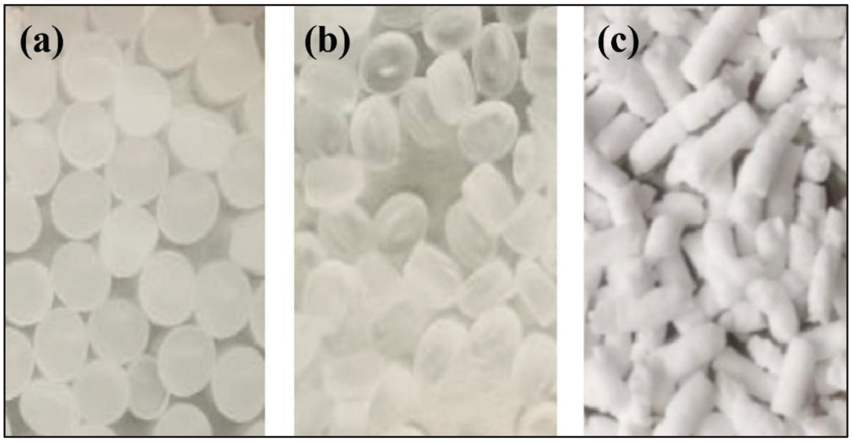


Figure 1.4 Polymer additives including (a) SBS, (b) EVA, and (c) LDPE
Taken from Hong et al. (2022)

Rubber additives, such as Crumb rubber derived from recycled tires, offer both performance and environmental benefits. It interacts with bitumen by absorbing lighter components, resulting in a modified binder with enhanced rutting resistance and reduced temperature susceptibility. Rubber-modified asphalt mixtures also reduce noise and maintenance costs, contributing to long-term sustainability (Ibrahim, Katman, Karim, Koting, & Mashaan, 2013; Navarro, Partal, Martínez-Boza, & Gallegos, 2005). Anti-stripping agents are chemical additives that improve adhesion between bitumen and aggregates, reducing moisture damage and enhancing the durability of asphalt mixtures (Nazirizad, Kavussi, & Abdi, 2015; Shu et al., 2022). Wax-based additives, such as Sasobit, play a crucial role in WMA technologies. At elevated temperatures, waxes reduce binder viscosity, facilitating lower mixing and compaction temperatures. At intermediate and lower temperatures, wax crystallization increases binder viscosity, improving rutting resistance. Wax additives also enhance workability, aging resistance, and fuel efficiency while reducing emissions (Jamshidi, Hamzah, & You, 2013; Şahan, Kumandaş, Kabadayı, Çavdar, & Oruç, 2023). Natural materials, such as lignin and bio-oils like soybean oil, are gaining traction as eco-friendly alternatives. Lignin, a bio-based by-product, aligns with sustainability goals by reducing reliance on petroleum-based binders. Bio-oils, often used as rejuvenators, contribute to enhancing bitumen properties and extending pavement life (Gaudenzi, Cardone, Lu, & Canestrari, 2023; R. Zhang, You, Ji, Shi, & Suo, 2021). In addition to these commonly used categories, other types of additives, including emerging materials and innovations, are continually being explored to address specific challenges in asphalt production.

Additives significantly influence the rheological behavior of bitumen, affecting its viscosity, elasticity, and responsiveness to temperature variations. They also alter thermal properties, such as softening point and ductility, enabling asphalt to perform effectively under diverse conditions. While additives enhance performance, sustainable options like crumb rubber and lignin help balance environmental impacts and production costs by promoting recycling and reducing reliance on non-renewable resources (Ameri & Ebrahimzadeh Shiraz, 2024; Tembe, Tamele Jr, Buonocore, Madivate, & Muiambo, 2023). Among the wide variety of additives employed in asphalt production, Sasobit and Kraft lignin are unique due to their distinctive properties and compatibility with sustainable practices. Given the focus of this study on these two materials, a deeper understanding of their mechanisms, effects on asphalt properties, and applications is essential to provide insights into their potential to advance modern asphalt technologies. The following sections examine Sasobit and Kraft lignin in detail.

1.5.1 Sasobit®

Sasobit® is a synthetic, long-chain aliphatic hydrocarbon compound commonly used as a WMA additive. Manufactured through the Fischer-Tropsch process, Sasobit differs from natural asphalt waxes due to its predominant hydrocarbon chain lengths, which range from 40 to 115 carbon atoms. It is available in various forms, such as flakes, prills (Figure 1.5), or pellets, and is typically added to asphalt binder or mixtures to enhance workability and reduce production temperatures. Sasobit melts between 70 and 120 °C and becomes fully miscible with asphalt binder at temperatures above 116 °C. Recommended dosages generally range from 0.8 to 4 % by mass of the binder, though many studies suggest limiting the amount to 3 % (Bilema et al., 2023; B. Chen et al., 2023; Hurley & Prowell, 2005; Jamshidi, Hamzah, & Zahed, 2013; R. Li, Shao, Yue, & Liang, 2023; J. Liu, Saboundjian, Li, Connor, & Brunette, 2011; W. Liu et al., 2023; Tembe et al., 2023).

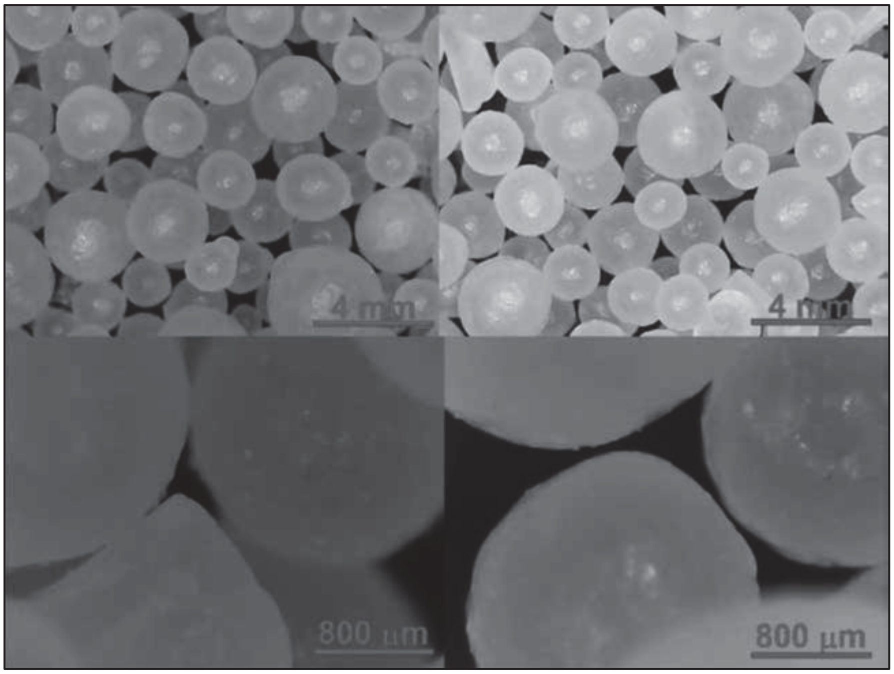


Figure 1.5 Microscope Images of Sasobit prills
Taken from Mousavi et al. (2017)

1.5.1.1 Functional Role and Interaction Mechanisms of Sasobit

At elevated temperatures, Sasobit functions as a viscosity reducer, enabling asphalt mixtures to be produced and compacted at significantly lower temperatures compared to traditional HMA. This reduction in production temperatures provides several advantages, including decreased energy consumption, lower greenhouse gas emissions, and a safer working environment due to reduced fume emissions. Additional benefits include an extended paving season, longer hauling distances, and faster road opening times. As the binder cools, Sasobit crystallizes to form a network-like structure, which increases viscosity at intermediate and lower temperatures (Hurley & Prowell, 2005; Zaumanis, 2014). This stiffening effect enhances the asphalt's resistance to rutting and deformation while maintaining its overall workability during production and application (Qin, Farrar, Pauli, & Adams, 2014).

1.5.1.2 Impact of Sasobit on Asphalt Performance Properties

Sasobit has a notable impact on various properties of asphalt binders and mixtures. It enhances rutting resistance at high service temperatures due to its stiffening effect, making asphalt more durable under heavy loads (Rathore & Soni, 2024). Additionally, some studies indicate that Sasobit improves fatigue resistance at intermediate temperatures, contributing to prolonged pavement life (Yue, Yue, Wang, & Xiong, 2021). While the additive generally has minimal influence on low-temperature performance, certain studies suggest a potential increase in susceptibility to low-temperature cracking, which warrants careful consideration during formulation (Jamshidi, Hamzah, & You, 2013). Sasobit may also slightly reduce moisture damage resistance in asphalt mixtures, emphasizing the need for an optimized mix design to mitigate this effect (Nabizadeh, Naderi, & Tabatabaee, 2017). Moreover, Sasobit is recognized for its ability to improve the aging resistance of asphalt binders, supporting longer pavement lifespans and enhancing overall durability (Jamshidi, Hamzah, & Aman, 2012).

1.5.1.3 Applications of Sasobit in Asphalt Mixture

Sasobit is widely employed in WMA technologies to lower mixing and compaction temperatures, establishing itself as a vital component in sustainable asphalt practices. It is particularly effective in reducing the high viscosity of rubber-modified asphalt, enabling production at standard temperatures and enhancing the practicality of such mixtures (Jiawei Zhu et al., 2024). Furthermore, Sasobit facilitates the incorporation of high percentages of RAP without compromising the workability of the mixture, making it a valuable additive in promoting sustainability and resource efficiency in asphalt production (Abdollahi, Karimi, Jahanbakhsh, & Tabatabaee, 2022).

1.5.2 Lignin

Lignin, a natural polymer and one of the most abundant biopolymers on Earth, has gained significant attention as a sustainable additive or extender for bitumen. Derived from various sources and extraction processes, lignin offers notable environmental benefits and performance enhancements while presenting certain challenges in its application within asphalt technologies. To fully understand these benefits, it is essential to consider the specific types and sources of lignin (Calvo-Flores, Dobado, Isac-García, & Martín-Martínez, 2015). Lignin content and composition vary significantly depending on the plant source, as illustrated in Figure 1.6.

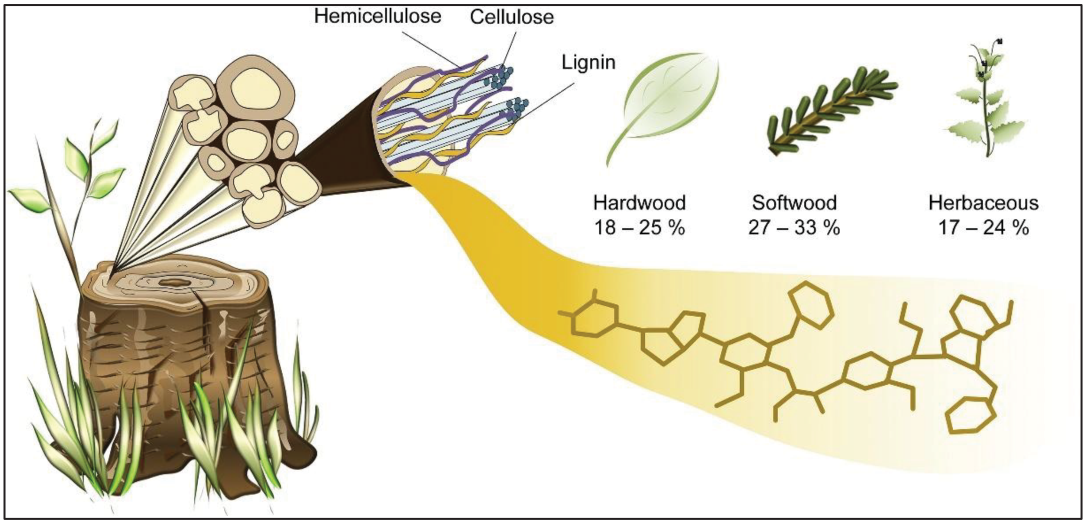


Figure 1.6 Lignin occurrence and composition in plants
Taken from Becker & Wittmann (2019)

The type and extraction method of lignin plays a crucial role in determining its chemical structure and properties, which directly influence its performance in bitumen modification. Kraft lignin, derived from the pulping process in the paper industry, is widely used in bitumen modification (Gaudenzi et al., 2023). Other sources of lignin include byproducts from biofuel production and agricultural residues, such as corn stalks, which further diversify its applications. However, the variability in lignin sources and extraction processes underscores the importance of careful selection and characterization to ensure consistent performance in asphalt mixtures.

Incorporating lignin into bitumen presents significant environmental and performance advantages, making it a promising additive or extender in asphalt applications. As a renewable material, lignin reduces reliance on petroleum-based binders and contributes to a lower carbon footprint during asphalt production, as shown in Figure 1.7.

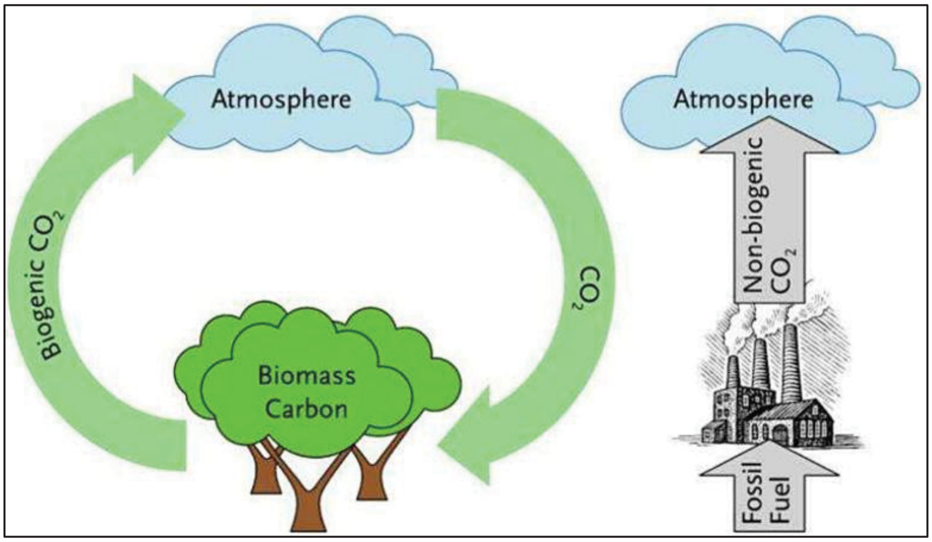


Figure 1.7 Comparison of biomass such as lignin and fossil fuel carbon cycles in the environment

Taken from Berndes et al. (2016)

Beyond environmental advantages, lignin also enhances several performance properties of bitumen. Lignin-modified bitumen demonstrates enhanced high-temperature performance. However, these improvements often necessitate higher mixing and compaction temperatures, which may offset some of the environmental benefits by increasing energy consumption. At low temperatures, lignin's effects are more variable, depending on its type, concentration, and source, as well as the characteristics of the base bitumen. While it can enhance flexibility and reduce thermal cracking in certain instances, increased stiffness in other cases may heighten susceptibility to cracking. In terms of rheological properties, lignin acts as a cross-linking agent, raising viscosity, which enhances the binder's performance across a wide range of temperatures. Additionally, lignin's antioxidant properties improve aging resistance. In terms of mechanical properties, lignin has been shown to improve properties such as Marshall Stability, moisture resistance, and rutting resistance in asphalt mixtures, contributing to their overall durability. However, the increased stiffness introduced by lignin may negatively impact fatigue life under repeated stress, making careful mix design and optimization essential to balance these effects and fully leverage lignin's potential (Gaudenzi et al., 2023; Tao et al., 2023; Yao et al., 2022).

Despite its promising benefits, lignin presents challenges that need to be addressed for optimized performance. The variability in chemical structures resulting from diverse extraction methods can lead to inconsistent results, complicating predictions and quality control. Storage stability is another concern, as lignin can segregate within bitumen at high temperatures, potentially affecting the uniformity and long-term performance of the binder. Additionally, the higher viscosity of lignin-modified bitumen can impact workability, requiring greater energy for mixing and compaction. These challenges highlight the need for further research to better understand the molecular interactions between lignin and bitumen components and to develop strategies for consistent and effective application (Gaudenzi et al., 2023; Yao et al., 2022).

1.5.2.1 Optimal Percentage of Lignin and its Proportional Impact

The incorporation of lignin in bitumen presents a complex interplay between its concentration and the resulting performance characteristics. While various studies have explored the effects of lignin content on bitumen properties, no universally optimal percentage has been established due to dependencies on factors such as the type of lignin, the source of bitumen, and the desired performance outcomes. Generally, lignin concentrations below 10 % are considered effective for balancing performance enhancements with acceptable drawbacks (Gaudenzi et al., 2023).

At lower concentrations (approximately 2–6 %), lignin primarily serves as a modifier, slightly enhancing specific bitumen properties without significantly altering its fundamental characteristics. Studies have shown that in this range, lignin can improve high-temperature performance by increasing the softening point, enhancing rutting resistance, and reducing temperature susceptibility. While there may be a slight increase in viscosity, workability typically remains acceptable. Additionally, lignin's antioxidant properties are evident even at low concentrations, contributing to improved aging resistance and reduced oxidation-related weight loss. Impacts on fatigue life and low-temperature performance are generally minor (Arafat, Kumar, Wasiuddin, Owhe, & Lynam, 2019; K. B. Batista et al., 2018; J. Wu, Liu, Wang, Wu, & Han, 2021; Xie, Li, Karki, Zhou, & Yuan, 2017; C. Xu et al., 2021; Yao et al., 2022; Y. Zhang et al., 2022).

As lignin concentration increases to moderate levels (6–10 %), its effects on bitumen properties become more pronounced. Significant improvements in high-temperature performance, aging resistance, and viscosity have been observed in this range. However, this concentration range may also introduce challenges, such as decreased ductility, increased stiffness, and potential brittleness, which could negatively affect fatigue life at higher strain levels. Low-temperature performance might be slightly impacted, although not dramatically (Arafat et al., 2019; K. B. Batista et al., 2018; J. Wu et al., 2021).

At higher concentrations (10–30 %), lignin can act as a bitumen extender, partially replacing the binder and potentially reducing material costs. However, the increased viscosity and stiffness necessitate higher mixing and compaction temperatures, which can offset some of the environmental benefits. While rutting resistance improves significantly, concerns about brittleness and susceptibility to low-temperature cracking become more prominent. Although lignin's antioxidant properties remain at these levels, the increased stiffness may paradoxically heighten the bitumen's vulnerability to oxidation and aging. Fatigue life is also likely to be adversely affected at high lignin concentrations (K. B. Batista et al., 2018; Hao Wang & Derewecki, 2013; J. Wu et al., 2021).

Studies suggest 6–9 % of lignin achieves a balance between benefits and drawbacks. However, the specific lignin type and source play a crucial role in determining its impact. For instance, Kraft lignin's effects on bitumen properties may differ from those of Organosolv lignin or other variants, necessitating careful consideration in the selection process (Gaudenzi et al., 2023). Excessive lignin content can result in overly stiff bitumen, reducing low-temperature performance and workability. Thus, optimizing lignin content involves balancing enhancing desired characteristics and mitigating potential limitations. A series of tests with varying lignin concentrations are recommended to evaluate the specific effects on bitumen properties and determine the most effective percentage for a given application.

1.5.2.2 Kraft lignin

Kraft lignin, a widely used type of lignin produced as a byproduct of the paper industry's pulping process (Figure 1.8), has garnered attention as a sustainable additive or extender for bitumen modification (Calvo-Flores et al., 2015). Its interaction with bitumen components significantly influences the material's rheological and mechanical properties, providing both advantages and challenges in asphalt applications (Argyropoulos et al., 2023).

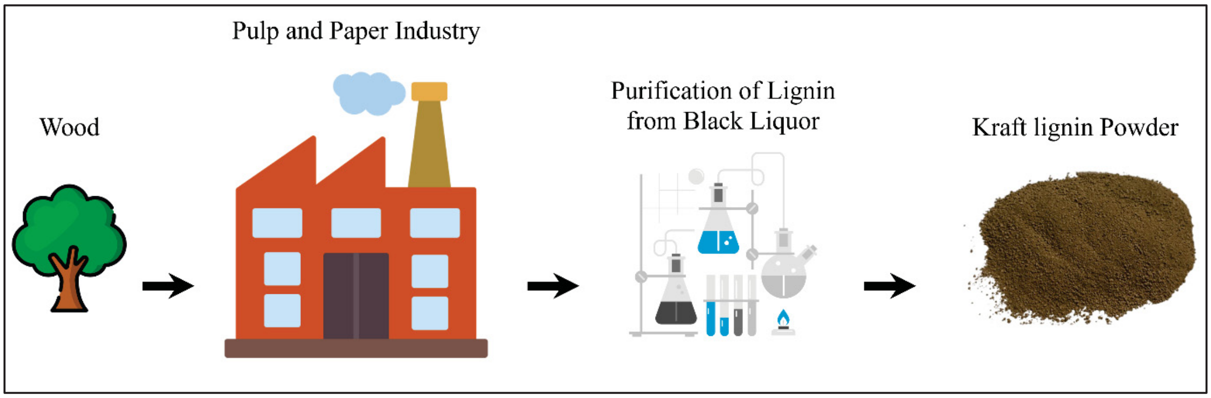


Figure 1.8 Kraft lignin production from the pulp and paper industry
Taken from Araújo et al. (2020)

One of the key effects of Kraft lignin on bitumen is its ability to increase viscosity (Gao et al., 2020; Gaudenzi et al., 2023). This effect is attributed to the interaction between Kraft lignin and the asphaltenes in the bitumen, where the lignin acts as a cross-linking agent (R. Zhang, Sun, et al., 2021). Higher viscosity contributes to better rutting resistance by stiffening the binder. However, it also necessitates higher mixing and compaction temperatures during construction, potentially offsetting some environmental benefits (K. B. Batista et al., 2018; C. Xu et al., 2021).

In addition to improving high-temperature performance, Kraft lignin enhances the aging resistance of bitumen (K. B. Batista et al., 2018; Tao et al., 2023; Xie et al., 2017). Acting as an antioxidant, it mitigates oxidation, a primary contributor to bitumen aging, by providing hydrogen and forming ketones that contain carbonyl groups. However, the interpretation of carbonyl indices using FTIR methods is complex, as these methods cannot distinguish between carbonyl groups originating from the binder and those formed by oxidized lignin (K. B. Batista et al., 2018). Despite this limitation, evidence supports the antioxidant properties of Kraft lignin, which can extend the lifespan of bitumen under aging conditions.

The effects of Kraft lignin on low-temperature performance are less consistent. While some studies suggest that lignin can improve flexibility and reduce stiffness at lower temperatures, thus decreasing thermal cracking susceptibility, others indicate the opposite (W. Wu, Li, Sevastyanova, Kringos, & Cavalli, 2024; C. Xu et al., 2021; R. Zhang, Sun, et al., 2021). In particular, increased stiffness and reduced flexibility at temperatures such as −18 °C have been associated with greater susceptibility to cracking (Cheng et al., 2020; Gaudenzi et al., 2023; Yu et al., 2021). These contradictory findings highlight the influence of factors such as Kraft lignin concentration, source, and the specific type of bitumen used (Arafat et al., 2019; Gaudenzi et al., 2023; R. Zhang, Sun, et al., 2021).

Kraft lignin's impact on fatigue performance presents another area of concern. Studies indicate that while low concentrations of lignin may have minimal effects, higher concentrations, such as 5 % or more, can significantly reduce fatigue life by increasing stiffness and brittleness (Gao et al., 2020; Gaudenzi et al., 2023; C. Xu et al., 2021). Interestingly, at 10 % lignin content, this negative effect on fatigue life appears to stabilize, particularly at higher strain levels, suggesting the potential for optimizing concentrations to balance performance and efficiency (G. Xu, Wang, & Zhu, 2017).

The variability in Kraft lignin's performance is further complicated by its source and extraction process. Differences in chemical structure, molecular weight, and functionality arising from diverse extraction techniques can result in inconsistent behavior when incorporated into bitumen (Argyropoulos et al., 2023; Yao et al., 2022). Additionally, storage stability issues, particularly at high temperatures, can lead to segregation of Kraft lignin in the binder, compromising the uniformity and long-term performance of modified bitumen (Gaudenzi et al., 2023).

Despite these challenges, Kraft lignin offers significant promise as a sustainable additive for bitumen, particularly in reducing reliance on petroleum-based products and enhancing high-temperature performance and aging resistance. However, to fully realize its potential, further research is essential to optimize lignin processing techniques and deepen the understanding of its interactions with bitumen components at a molecular level. Addressing these challenges will be critical in maximizing Kraft lignin’s capabilities as a sustainable alternative in asphalt applications.

1.6 Blending Additives with Bitumen

Achieving uniform dispersion of additives in bitumen is essential for ensuring consistent performance and optimal properties of the modified binder. Blending parameters, including temperature, time, and rate, play a crucial role in determining the efficiency of additive incorporation and the final product's performance (Arafat et al., 2019; A. M. Memon, Sutanto, Napiah, Khan, & Rafiq, 2020; Stimilli, Ferrotti, Conti, Tosi, & Canestrari, 2014; N. S. A. Yaro, Napiah, Sutanto, Usman, & Saeed, 2021). Different additives require specific blending conditions to achieve their desired effects, as their chemical and physical properties influence their interaction with bitumen. For example, polymer-modified bitumen exhibits dual-phase morphology, making it critical to optimize blending conditions to ensure storage stability and prevent phase separation under high temperatures and prolonged storage (Saboo & Kumar, 2016).

1.6.1 Blending Temperature

The temperature must be high enough to ensure proper mixing and dispersion without degrading the bitumen or additives. Insufficient temperatures can result in poor mixing, leading to phase separation and inconsistent performance, while excessive temperatures can cause oxidation of bitumen, affecting its rheological properties. The optimal blending temperature varies with the additive type but typically ranges between 130 and 180 °C, depending on the specific requirements of the modification process (K. B. Batista et al., 2018; A. M. Memon et al., 2020; Saboo & Kumar, 2016; Stimilli et al., 2014; N. Yaro et al., 2022; N. S. A. Yaro et al., 2021).

1.6.2 Blending Rate and Equipment

The choice of blending equipment and rate significantly affects the efficiency of mixing and the uniform distribution of additives. High-shear mixers are generally preferred for their ability to generate the necessary forces to disperse additives uniformly, creating a more homogeneous mixture (R. Zhang, Sun, et al., 2021). However, these mixers must be carefully controlled to avoid excessive oxidation or degradation of additives. Mechanical mixers, while less efficient, can be suitable for specific applications, particularly when lower shear rates are sufficient (K. B. Batista et al., 2018). The blending rate also depends on the additive type. Bio-based additives, such as lignin often require high shear rates to break down particles and ensure uniform dispersion (Ren et al., 2021). Conversely, synthetic additives may require different blending rates based on product-specific recommendations. These considerations highlight the need to adjust blending processes to the additive's characteristics and the intended application (A. M. Memon et al., 2020; N. S. A. Yaro et al., 2021).

1.6.3 Blending Time

Blending time is another critical parameter that influences the homogeneity and stability of the modified bitumen. Sufficient mixing time ensures the even dispersion of the additive throughout the bitumen matrix, enhancing the binder's performance (K. B. Batista et al., 2018; A. M. Memon et al., 2020). However, prolonged mixing can lead to increased energy consumption and potential degradation of bitumen or additives, emphasizing the need for balancing efficiency and stability (Mashaan & Karim, 2013; Özdemir, Topal, & Sengoz, 2020).

1.6.4 Blending Lignin with Bitumen

The blending of lignin with bitumen presents unique challenges and requires specific parameters to achieve optimal results. Lignin is typically blended at temperatures ranging from 130 to 180 °C, using high-shear mixers operating at speeds of 3000 to 5000 rpm. Blending times generally vary between 30 and 60 minutes to ensure adequate dispersion (Al-falahat, Lamothe, Carret, & Carter, 2024; Arafat et al., 2019; K. B. Batista et al., 2018; Gao et al., 2020; Ren et al., 2021; G. Xu et al., 2017; Zarei, Zarei, & Janmohammadi, 2019; R. Zhang, Sun, et al., 2021). However, lignin’s tendency to agglomerate can reduce homogeneity, necessitating precise control of blending conditions to mitigate this issue. Kraft lignin has been shown to integrate well with bitumen when blended at up to 30 % by weight without compromising storage stability or homogeneity (Al-falahat et al., 2024). Comparisons with other lignin types are limited, but the specific properties of Kraft lignin make it particularly suitable for bitumen modification (R. Zhang, Sun, et al., 2021).

The blending of single additives with bitumen has been extensively studied, but the simultaneous incorporation of multiple additives remains less understood. Additive combinations can result in synergistic or anti-synergistic effects, impacting the physical and rheological properties of the modified binder. Further research is needed to investigate these interactions and optimize blending techniques to maximize the full potential of additive combinations in bitumen modification.

1.7 Properties of Modified Bitumen

Investigating the properties of modified bitumen reveals insights into its behavior, enabling the potential for enhancements in performance and durability in diverse asphalt applications. Understanding the properties of modified bitumen requires an in-depth examination of various advanced testing methods. This section delves into rheological, chemical, thermal, and microscopic characteristics, focusing on the testing methods employed in this research to assess these properties. These methodologies provide critical insights into the influence of various additives, such as lignin and Sasobit, on the properties and performance of modified bitumen.

1.7.1 Rheological Properties

Rheological properties are critical to evaluating the performance of bitumen, particularly under varying temperatures and loading conditions. The viscoelastic behavior of bitumen is analyzed through multiple techniques that provide valuable insights into its suitability for asphalt applications.

The Brookfield Rotational Viscometer (BRV) measures the viscosity of bitumen by rotating a cylindrical spindle within a container of bitumen. The torque required to maintain a steady spindle rotation provides a measure of viscosity, which directly impacts the workability of bitumen during asphalt production. For instance, optimal viscosity ensures efficient pumping, mixing with aggregates, and compaction of asphalt mixtures.

Dynamic Shear Rheometer (DSR) evaluates the viscoelastic properties of bitumen by measuring the complex shear modulus (G^*) and phase angle (δ). G^* represents the material's resistance to deformation, while δ reflects the balance between elastic and viscous behavior. These parameters are crucial for predicting rutting resistance at high temperatures and fatigue performance under repeated traffic loads.

The Multiple Stress Creep Recovery (MSCR) test provides insights into the non-recoverable creep compliance (J_{nr}) and recovery percentage of bitumen, essential for characterizing its resistance to permanent deformation.

For low-temperature performance, the Bending Beam Rheometer (BBR) is used to evaluate stiffness and relaxation properties, critical for assessing susceptibility to thermal cracking. This test ensures that bitumen can resist cold weather conditions without becoming excessively brittle, thus maintaining the pavement's structural integrity in adverse climates. These rheological testing methods collectively contribute to understanding the complex behavior of bitumen and optimizing its performance in diverse environments. (Speight, 2015).

1.7.2 Chemical Reactions with Additives

Chemical analysis provides insights into the interactions between bitumen and additives. Fourier-Transform Infrared Spectroscopy (FTIR) is extensively used to study these reactions. By analyzing functional group changes, FTIR can detect oxidation, aging, and the incorporation of various modifiers like polymers or bio-based additives (Gómez, Oeser, & Fleischel, 2021; Nivitha, Prasad, & Krishnan, 2019; D. Zhang et al., 2022; Zofka, Maliszewska, Maliszewski, & Boratyński, 2015).

1.7.3 Thermal Properties

Understanding the thermal properties of modified bitumen is used for evaluating its stability and performance under temperature variations. Thermal characterization methods provide valuable insights into the material's behavior during production, application, and throughout its service life.

Thermogravimetric Analysis (TGA) is commonly used to assess the thermal stability and decomposition patterns of bitumen. This technique measures weight loss as a function of temperature, offering insights into the volatilization of lighter components, the breakdown of heavier fractions. The results highlight bitumen's high-temperature performance, making it possible to identify how additives or modifications influence its thermal stability. The use of TGA has also been expanded to analyze the evolved gases during decomposition, providing a deeper understanding of bitumen's thermal degradation mechanisms and their environmental implications (Elkashef, Williams, & Cochran, 2018; Fiedlerova, Jíša, Kadlec, Velvarská, & Štěpánek, 2021; Lucena, Soares, & Soares, 2004; J. Zhang, Wang, Wu, Sun, & Wang, 2009).

Differential Scanning Calorimetry (DSC) complements TGA by quantifying thermal transitions such as the glass transition temperature (T_g). These transitions are crucial for assessing the flexibility of bitumen, its susceptibility to thermal cracking, and the compatibility of various additives (Dong, Zhao, & Tang, 2019; Fang, Liu, Yu, & Liu, 2014; Kaya, Topal, Gupta, & McNally, 2020; Motamedi, Attar, & Rostami, 2017).

1.7.4 Microscopic Properties

Microscopic analysis techniques provide insights into the microstructural characteristics of bitumen, allowing researchers to understand the distribution and interaction of additives within the binder matrix. Among the various techniques available, Environmental Scanning Electron Microscopy (ESEM) is unique for its ability to observe bitumen in its natural state without extensive sample preparation. Unlike conventional Scanning Electron Microscopy (SEM), ESEM operates under a controlled environment, enabling the examination of wet, oily, or non-conductive samples, which are often challenging to analyze.

ESEM is particularly effective for studying the morphology and distribution of additives in bitumen, as well as phase separation and microstructural features such as fibril networks. These capabilities make it a valuable tool for understanding how additives influence the mechanical and rheological properties of bitumen. Although its application is not widely employed for lignin or Sasobit blends, ESEM has proven effective in analyzing polymer- and crumb rubber-modified binders, providing valuable insights into additive dispersion and interaction (P Lin et al., 2021; Lu, Sjövall, Soenen, & Andersson, 2018; Pipintakos, Hasheminejad, Lommaert, Bocharova, & Blom, 2021).

1.8 Synergistic Effects of Additives

1.8.1 Synergistic Effects of Sasobit with Other Additives

The incorporation of Sasobit demonstrates significant synergistic effects when combined with other asphalt modifiers, enhancing both performance and sustainability. Its role as a secondary modifier has been studied in combination with various types of modified bitumen, demonstrating its ability to address specific challenges and optimize mixture properties. The following sections highlight some studies and findings on the interactions between Sasobit and commonly used asphalt modifiers.

1.8.1.1 Sasobit and Rubber Additives

Sasobit exhibits notable synergies when combined with crumb rubber (Jamshidi, Hamzah, & You, 2013). The addition of Sasobit reduces the viscosity of rubberized asphalt binders at high temperatures, enabling lower mixing and compaction temperatures. Furthermore, the reduction of mixing and compaction temperatures of rubberized asphalt mixes from 173 and 155 °C to approximately 150 and 140 °C, respectively, have been reported (Xiao, Zhao, & Amirkhanian, 2009). This decrease not only minimizes fuel consumption and greenhouse gas emissions but also enhances the environmental footprint of rubberized asphalt. Additionally, Sasobit improves the performance characteristics of rubberized asphalt mixtures, including decreased permanent deformation potential and increased softening points, stiffness, and fatigue resistance. However, the extent of these improvements depends on factors such as the crumb rubber content, mesh size, Sasobit dosage, and the source of the asphalt binder (Akisetty, Gandhi, Lee, & Amirkhanian, 2010; Akisetty, Lee, & Amirkhanian, 2010; M. Li, Lv, Ran, & Li, 2011; Z. Zhang, Wu, & Zhao, 2011).

1.8.1.2 Sasobit and Polymer-Modified Asphalt

Sasobit also interacts positively with polymer-modified binders, such as those modified with styrene-butadiene-styrene (SBS) or ethylene-vinyl acetate (EVA) (Jamshidi, Hamzah, & You, 2013). By lowering the viscosity of these binders, Sasobit facilitates reduced construction temperatures, contributing to cost savings and a reduced environmental impact (Z. Li, Lu, Liu, & Wang, 2024). Moreover, Sasobit enhances the storage stability of polymer-modified binders, mitigating common issues such as phase separation and ensuring a homogenous dispersion of polymers (Edwards, Tasdemir, & Butt, 2010; Ho, Macleod, & Zanzotto, 2008). However, while Sasobit improves the workability and storage stability of polymer-modified asphalt, it may also increase the stiffness and complex shear modulus (G*), which should be carefully considered during mix design (Hajj, Souliman, & Cortez, 2014).

1.8.1.3 Sasobit and High-RAP Mixtures

The use of Sasobit in mixtures containing high percentages of RAP has shown promising results (Jamshidi, Hamzah, & You, 2013). By reducing the viscosity of aged binders in RAP, Sasobit allows for lower construction temperatures without compromising mixture workability. This facilitates the incorporation of higher RAP content, aligning with sustainability goals by reducing the reliance on virgin materials and lowering energy consumption (Amini & Parvizi, 2024). Studies indicate that high-RAP mixtures with Sasobit exhibit improved compactability and comparable or enhanced performance compared to conventional mixtures. However, vulnerability to fatigue and low-temperature cracking, potentially due to higher binder stiffness, is reported (Mondal, Islam, & Ransinchung RN, 2023).

The use of Sasobit in combination with other modifiers demonstrates its potential to advance sustainable asphalt technologies. By lowering production and compaction temperatures, Sasobit reduces energy consumption and greenhouse gas emissions, particularly when integrated with polymer-modified bitumen and recycled materials like RAP and crumb rubber.

These reductions in energy demand not only contribute to sustainability but also support the industry's goals for cost efficiency. Sasobit's unique interactions with rubber additives, polymers, and recycled materials demonstrate its adaptability in improving asphalt mixture performance. These synergies enhance workability, extend the application of high-recycled-content mixtures, and mitigate specific challenges, such as viscosity management. By enabling innovative approaches to asphalt production, Sasobit is a key additive in developing high-performance, environmentally sustainable pavement solutions.

1.9 Asphalt Mix Design

The design of asphalt mixtures is the foundation of pavement engineering, aimed at achieving durability, stability, and optimal performance under diverse traffic loads and environmental conditions. Over decades, various mix design methods have been developed, each catering to specific requirements. This section outlines key mix design approaches, emphasizing their methodologies and applications.

One of the earliest and most widely used methods is the Marshall mix design, introduced by Bruce Marshall in 1939. This method focuses on creating a durable mix with an optimal air void content, generally around 4 %, while minimizing asphalt binder use. The process involves selecting aggregates and asphalt binder, preparing specimens with varying binder contents, compacting them with a Marshall hammer, and evaluating critical properties such as stability, flow, density, and volumetric characteristics. Known for its simplicity, the Marshall method is particularly suited for regions with lower traffic volumes.

Another notable approach is the Hveem mix design, developed by Francis Hveem in the 1930s. This method prioritizes stability, cohesion, and durability by ensuring adequate binder coating on aggregates to promote long-term performance. Specialized equipment, such as the Hveem Stabilometer, is used to evaluate stability, while the Cohesiometer measures cohesion. While its use has declined, the Hveem method remains applicable in regions with specific performance demands.

The Superpave (Superior Performing Asphalt Pavement) method, developed under the Strategic Highway Research Program (SHRP), represents a performance-driven approach. It integrates the selection of performance-graded (PG) asphalt binders and aggregates with compaction using the Superpave Gyratory Compactor (SGC). Superpave evaluates mix properties under targeted traffic and environmental conditions, using compaction effort levels ($N_{initial}$, N_{design}, and N_{final}). Its adaptability to high-traffic roads and diverse climates has made it a preferred choice in modern infrastructure projects.

The LC Method, developed by Quebec's Ministry of Transportation (MTQ), has a hybrid approach, incorporating elements of both the Superpave system and the French mix design method (LCPC: Laboratoire Central des Ponts et Chaussées). As shown in Figure 1.9, this method focuses on calculating asphalt content based on the volume of effective asphalt cement (V_{be}), eliminating Conventional metrics such as voids in mineral aggregate (VMA) and voids filled with asphalt (VFA). This method streamlines the design process while achieving optimal binder distribution and volumetric properties, making it effective for specialized regional applications (McGennis, Anderson, Kennedy, & Solaimanian, 1995; Roberts, Mohammad, & Wang, 2002).

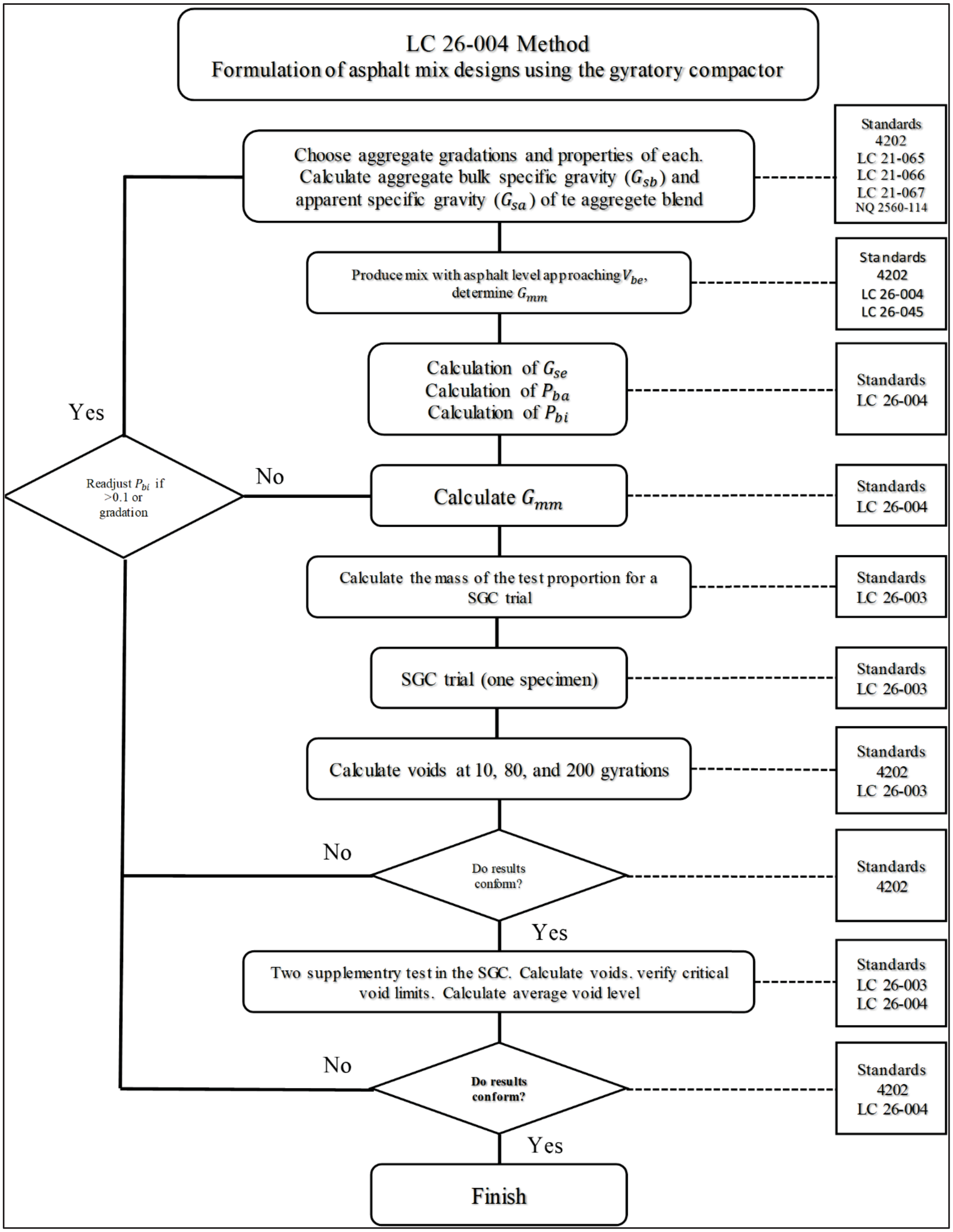


Figure 1.9 LC mix design flowchart

Taken from Carter et al. (2018)

1.10 Production Temperatures and Energy Efficiency

Optimizing production temperatures has emerged as a pivotal strategy in the asphalt industry’s efforts toward sustainability. Traditional HMA production requires high temperatures for mixing and compaction, leading to significant energy consumption and greenhouse gas (GHG) emissions. Lowering these temperatures offers substantial energy savings and a reduced environmental footprint, making it a critical focus area in modern asphalt practices (Rubio, Martínez, Baena, & Moreno, 2012; Thives & Ghisi, 2017).

WMA technologies represent a transformative approach, enabling lower mixing and compaction at temperatures than conventional HMA. This reduction is achieved through methods such as the use of organic additives, chemical agents, and foaming techniques (Abed, Thom, & Grenfell, 2019; Oliveira, Silva, Abreu, & Fernandes, 2013). The benefits of WMA technologies extend across environmental, economic, and performance dimensions. By reducing energy consumption during production by up to 18 % and GHG emissions by approximately 33 %, WMA significantly mitigates the environmental impact of asphalt production (Almeida-Costa & Benta, 2016; Blankendaal, Schuur, & Voordijk, 2014). Some studies highlight energy savings of 20–70 % and CO_2 emission reductions exceeding 75 % for specific road applications (Kristjansdottir, 2006; Thives & Ghisi, 2017). Additionally, improved compaction and workability at lower temperatures reduce the effort required to achieve target densities, allowing for extended paving seasons and paving under colder conditions (Sukhija, Wagh, & Saboo, 2021). WMA mixtures also exhibit reduced binder hardening during production and achieve improved in-situ densities, resulting in performance comparable to or exceeding that of traditional HMA (C. Wang, Hao, Ruan, Zhang, & Adhikari, 2013). The reduced production temperatures facilitate the incorporation of higher percentages of RAP, enhancing sustainability by minimizing reliance on virgin materials (Abed, Thom, & Lo Presti, 2018; K. Zhang, Huchet, & Hobbs, 2019).

Despite these advancements, challenges remain. The integration of lignin as a bio-based additive presents potential viscosity increases that necessitate higher mixing and compaction temperatures, which may offset some energy savings. While Sasobit enhances workability and reduces energy demands, the combination of Sasobit and Kraft lignin could yield synergistic benefits, such as improved aging resistance and environmental sustainability. However, further research is required to fully understand their interactions and optimize their combined effects on energy efficiency and asphalt performance. Lowering production temperatures remains a key component of sustainable asphalt practices. Innovations like WMA technologies, combined with bio-based additives, offer a pathway to reduced energy consumption, lower emissions, and enhanced performance. Addressing challenges related to additive integration and compatibility will be crucial for advancing these approaches and achieving a more sustainable asphalt industry.

1.11 Summary and Research Perspective

This literature review provides a comprehensive foundation for understanding the critical aspects of asphalt production, bitumen modification, and sustainability in pavement engineering. The focus on key topics such as the types of asphalt mixes, sustainable practices, and the role of additives like Sasobit and lignin offers a cohesive framework to address modern challenges in the asphalt industry. By emphasizing the environmental impacts of conventional methods and the potential of innovative technologies, this review underscores the importance of adopting sustainable approaches in asphalt production.

The review also highlights significant knowledge gaps and research opportunities, particularly in the synergistic use of additives like Sasobit and Kraft lignin. While both additives demonstrate promising benefits in improving asphalt properties and reducing environmental impacts, a comprehensive understanding of their combined effects on the physical, chemical, and rheological behavior of asphalt remains underexplored. This gap forms the core of this thesis, which seeks to bridge the divide between experimental findings and practical applications. Through the systematic investigation of blending conditions, chemo-thermal properties, and asphalt mix characteristics, this research aims to contribute to the development of innovative, sustainable, and high-performance asphalt technologies.

CHAPTER 2

RESEARCH OBJECTIVE AND EXPERIMENTAL PLAN

2.1 Introduction

The primary objective of this PhD research was to advance the understanding and application of sustainable additives or modifiers in Warm Mix Asphalt (WMA) technologies, focusing on enhancing the environmental and performance characteristics of asphalt. The project was initially designed to investigate the potential of Aluminosilicate additives for WMA. However, as the research progressed, experimental findings necessitated a strategic shift toward Kraft lignin, a bio-based polymer, due to its promising properties and alignment with the sustainability objectives of asphalt technology. The revised objective for Kraft lignin was to evaluate its potential as sustainable additive ore replaced and contribute to the broader sustainability goals of asphalt technologies.

This chapter presents a comprehensive overview of the evolution of research objectives, the reasons for the significant shift, and the systematic experimental framework developed to address the revised goals. The research was conducted in distinct phases, each with specific objectives, methodologies, and outcomes, which are detailed in this chapter. Figure 2.1 shows the overview of the experimental plan and research framework which visually summarizing the research plan and methodology.

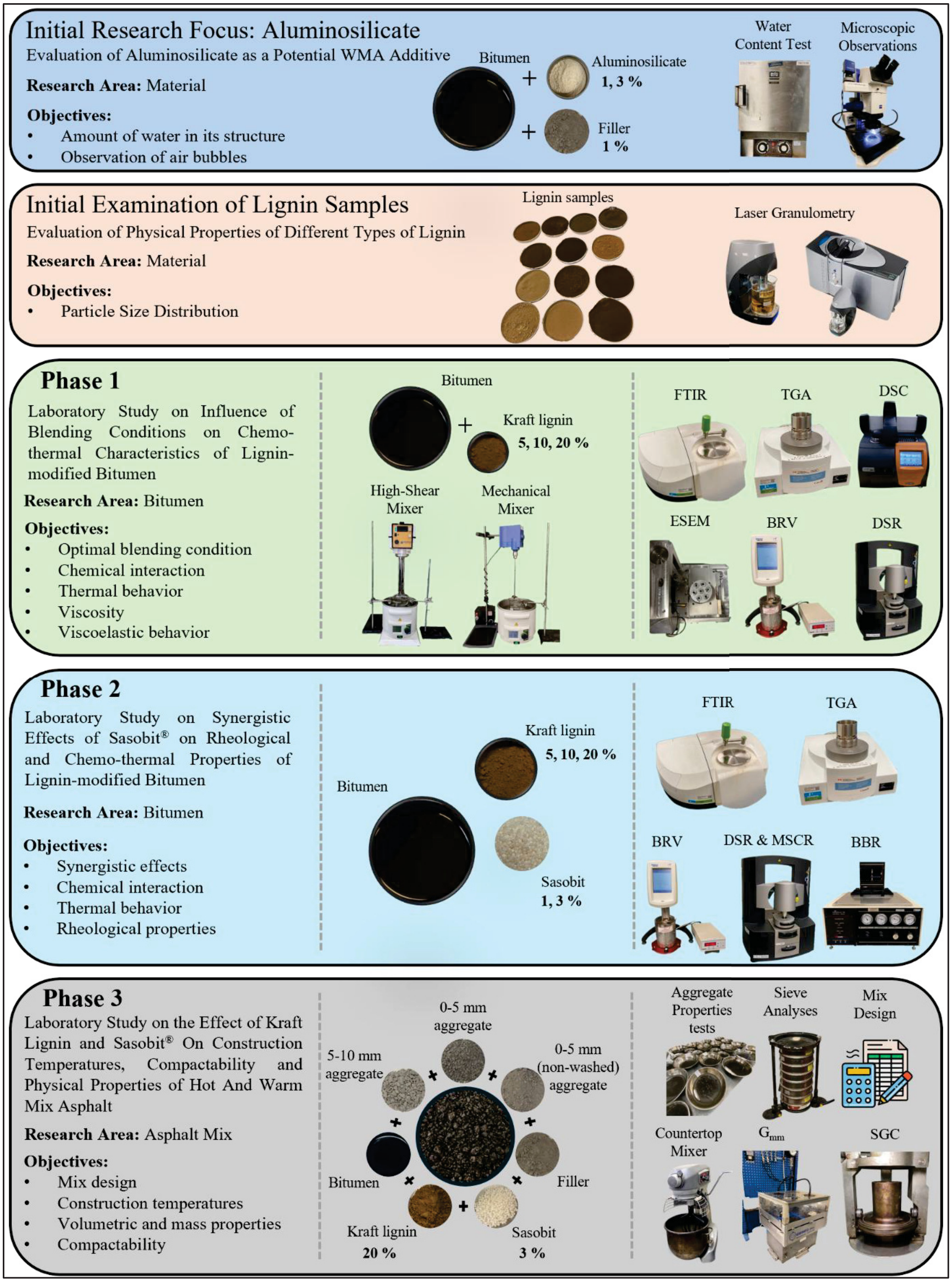


Figure 2.1 Overview of the Experimental Plan and Research Framework

2.2 Initial Research Focus on Aluminosilicate Additives

The research initially focused on investigating Aluminosilicate, a specific type of zeolite, as a potential WMA modifier. Supplied by Corporation Nemaska Lithium Inc. as a byproduct of the lithium production process, Aluminosilicate was provided in the form of a fine white powder. According to the literature, Aluminosilicate has been reported to lower mixing and compaction temperatures while enhancing the workability of asphalt mixtures when used as a WMA additive. A comprehensive experimental plan was designed in four phases to investigate the properties and impacts of this additive on asphalt performance. These phases included: characterizing Aluminosilicate and determining its optimal dosage, evaluating its role as a filler material, assessing the mechanical properties of WMA incorporating Aluminosilicate, and analyzing the rheological properties of binders extracted from Aluminosilicate-modified asphalt mixes. This framework was outlined in the research proposal. However, during the first phase, which included initial laboratory tests and analysis, the results revealed significant gaps between the observed properties of Aluminosilicate and the findings reported in the existing literature. These unexpected results indicated that the properties of the additive did not align with the project's performance and sustainability objectives. Consequently, the decision was made to shift the research focus to an alternative sustainable additive.

2.3 Transition to Lignin as a Sustainable Material

The strategic transition from Aluminosilicate to Kraft lignin as the primary research focus necessitated the establishment of a new objective that aligned with the sustainability goals and performance requirements of modern asphalt technologies. This shift was motivated by the inherent limitations observed in the initial research on Aluminosilicate and the promising potential of lignin as a bio-based polymer and its potential to improve bitumen and asphalt mix properties.

The primary objective of the revised research plan became the systematic evaluation of Kraft lignin's potential as a sustainable additive for asphalt modification. This revised focus allowed the research to address critical knowledge gaps in the application of bio-based additives in asphalt technology, offering innovative solutions for balancing sustainability with performance. By framing lignin as a central component of this study, the research aimed to contribute to developing environmentally responsible asphalt technologies that meet the demands of modern infrastructure.

2.3.1 Initial Examination of Lignin Samples

Lignin is derived from various sources and production processes, such as Kraft pulping, which affect its chemical structure and applicability in asphalt modification. Collaborating with a lignin supplier, sixteen (16) different lignin samples were initially provided, representing variations in source and processing methods. The initial stage of the lignin-based project focused on evaluating the physical properties of these lignin samples. Particle Size Distribution (PSD) tests were performed to assess the size and uniformity of the lignin particles. Based on the test results from previous studies, the supplier's resource availability, production processes, and recommendations regarding feasibility, a specific type of lignin was selected for further investigation.

2.4 Comprehensive Experimental Framework

Following the selection of a specific lignin type called Kraft lignin, the research was divided into three distinct phases, each aimed at investigating critical aspects of lignin properties, the challenges associated with its incorporation into bitumen, and its application in asphalt mixtures. Additionally, innovative solutions were proposed to address some of the challenges by incorporating a secondary additive, Sasobit®, into bitumen and asphalt mixtures. These phases formed the foundation of the research, resulting in the publication of three scientific journal articles.

2.4.1 Phase 1: Investigation of Blending Conditions and Chemo-Thermal Properties of Lignin-Modified Bitumen

2.4.1.1 Objective

The primary objective of the first phase of this research was to establish optimal blending conditions for incorporating Kraft lignin into bitumen. A critical question guiding this phase was whether high-shear mixing (HSM) or conventional mechanical mixing (MM) would be more effective for ensuring uniform dispersion of lignin in the bitumen matrix.

In addition, this phase aimed to investigate the thermal behavior of lignin-modified bitumen. Given the high temperatures involved in asphalt production, understanding the thermal stability and decomposition patterns of the modified binder was essential. The interactions between bitumen and lignin, including the chemical compatibility and visual insights and potential bonding mechanisms, were also of significant interest, as they directly influence the performance and durability of the binder.

Another key objective was to evaluate the impact of Kraft lignin on the viscosity of bitumen, a critical factor affecting production temperatures and workability. Finally, the viscoelastic behavior of lignin-modified bitumen was examined to understand its performance under varying temperature conditions.

These comprehensive objectives collectively defined the scope of this phase, laying the groundwork for systematically evaluating the physical, rheological, and thermal properties of lignin-modified bitumen.

2.4.1.2 Methodology

To achieve the objectives of this phase, a detailed experimental methodology was designed and implemented. The study followed a structured approach to evaluate the blending conditions and the resulting physical, rheological, and chemo-thermal properties of lignin-modified bitumen.

The samples were prepared with Kraft lignin concentrations of 5, 10, and 20 %. Two distinct blending methods were employed to compare their effectiveness including a high-shear mixer (HSM) and a mechanical mixer (MM) to evaluate their relative efficiency.

Viscosity testing of the lignin-modified bitumen was performed using the Brookfield Rotational Viscometer (BRV). This test measured viscosity at various temperatures, providing insights into the workability of the modified binder during production and application. Dynamic Shear Rheometer (DSR) was employed to investigate rheological properties by measuring the complex shear modulus (G*) and phase angle (δ). These parameters provided insights into the viscoelastic behavior of lignin-modified bitumen. Chemical and thermal characterization included a range of advanced techniques. Fourier Transform Infrared Spectroscopy (FTIR) was used to detect chemical interactions between lignin and bitumen by identifying changes in functional groups. Thermogravimetric Analysis (TGA) assessed the thermal stability and decomposition behavior of the modified bitumen, while Differential Scanning Calorimetry (DSC) evaluated thermal transitions, such as the glass transition temperature (T_g), to determine the compatibility of lignin with bitumen. Microscopic analysis was conducted using Environmental Scanning Electron Microscopy (ESEM), which provided visual insights into the dispersion and morphology of lignin particles within the bitumen matrix. This analysis was critical for assessing the uniformity of dispersion achieved by the two blending methods.

The results of this phase provided significant insights into the influence of blending conditions on the Physical, Rheological, and chemo-thermal properties of lignin-modified bitumen. The comparison between the two mixing protocols demonstrated the importance of shear forces in achieving uniform dispersion, which directly affected the different properties of the binder. These findings not only established a foundational understanding of the blending behavior of lignin with bitumen but also provided critical guidance for the subsequent phases of the research. These results were published in the first article, *"Laboratory Study on Influence of Blending Conditions on Chemo-Thermal Characteristics of Lignin-Modified Bitumen"*.

2.4.2 Phase 2: Synergistic Effects of Sasobit and Kraft lignin on Bitumen Properties

2.4.2.1 Objective

The second phase of the research aimed to address the challenges faced in lignin-modified bitumen produced during the first phase by incorporating Sasobit as a WMA additive. This phase also focused on investigating the synergistic effects arising from the combined use of Kraft lignin and Sasobit for bitumen modification. Specifically, it aimed to examine how adding Sasobit could mitigate the viscosity increase observed in lignin-modified bitumen while enhancing its thermal and rheological performance.

The key objectives of this phase focused on evaluating the synergistic effects resulting from the combined use of Kraft lignin and Sasobit as bitumen modifiers. This involved a comprehensive investigation into the chemo-thermal and rheological properties of bitumen modified. A primary objective was to assess how the introduction of Sasobit as a secondary additive could effectively reduce the viscosity of lignin-modified bitumen, thereby improving its workability and construction temperatures.

Another critical objective was to evaluate the viscoelastic behavior of the modified binders under high-temperature conditions, with a particular focus on deformation resistance and rutting performance. Additionally, the thermal stability and chemical interactions between lignin, Sasobit, and bitumen were analyzed using advanced characterization techniques to gain insights into the stability and compatibility of the modified system.

The susceptibility of the modified bitumen to thermal cracking under low temperatures was also aimed to ensure its performance in a broader range of environmental conditions. By incorporating Sasobit, this phase introduced an additional layer of complexity to the research, enabling a more comprehensive understanding of the interactions between these two sustainable additives and their overall impact on the performance of bitumen.

2.4.2.2 Methodology

A structured experimental framework was developed to investigate the combined effects of Kraft lignin and Sasobit on bitumen properties. This phase involved the production of 13 distinct bitumen samples, containing a range of individual and combined additive concentrations. Specifically, 5, 10, and 20 % concentrations of Kraft lignin and 1 and 3 % Sasobit were incorporated, both individually and in combination, to assess their individual and synergistic effects on bitumen performance.

To evaluate the influence of these additives, a comprehensive series of chemical, thermal, and rheological tests were performed. For thermal and chemical characterization, Fourier Transform Infrared Spectroscopy (FTIR) was used to evaluate chemical interactions by detecting changes in functional groups, while Thermogravimetric Analysis (TGA) was employed to evaluate the thermal stability and decomposition behavior of the modified binders.

The rheological properties of the samples were analyzed through multiple advanced techniques. The Brookfield Rotational Viscometer (BRV) was used to measure viscosity. The Dynamic Shear Rheometer (DSR) was employed to investigate the viscoelastic properties of the binders, including complex shear modulus ($|G^*|$) and phase angle (δ). The Multiple Stress Creep Recovery (MSCR) test was conducted to measure deformation resistance and elasticity under cyclic loadings. Low-temperature performance was assessed using the Bending Beam Rheometer (BBR), which analyzed the thermal cracking susceptibility of the modified bitumen by measuring creep stiffness and relaxation rates at sub-zero temperatures.

The results from the rheological, thermal, and chemical analyses were integrated to identify optimal concentrations of Kraft lignin and Sasobit that enhance bitumen performance. This comprehensive analysis provided a deeper understanding of the interactions between these additives and their collective influence on bitumen properties.

This phase of the study resulted in the publication of a research article in the International Journal of Road Materials and Pavement Design (RMPD), a Q1-ranked journal, under the title *"Laboratory Study on Synergistic Effects of Sasobit® on Rheological and Chemo-Thermal Properties of Lignin-Modified Bitumen."* This publication highlights the significance of the findings and their contribution to developing sustainable asphalt technologies.

2.4.3 Phase 3: Evaluating the Influence of Lignin and Sasobit on Physical Properties Asphalt Mix and Construction Temperatures

2.4.3.1 Objective

The third and final phase of the research aimed to shift from laboratory-scale binder studies to the production and evaluation of asphalt mixtures. This phase represents a critical step toward practical implementation, focusing on the mix design and evaluation of both HMA and WMA incorporating Kraft lignin and Sasobit. The main objective was to evaluate the feasibility of integrating these bio-based and viscosity-reducing additives into asphalt mixtures. This phase aimed to investigate how the combined use of Kraft lignin and Sasobit affects key volumetric and mass properties of the mix, compaction behavior, and construction temperatures.

One of the key objectives of this phase was the development of a comprehensive mix design for HMA and WMA, which included the necessary calculations and design parameters for mixes containing Kraft lignin, Sasobit, and their combination. The next objective was to optimize construction temperatures by determining the impact of Kraft lignin, Sasobit, and their combined use on the required production and compaction temperatures for both HMA and WMA. Another objective was to investigate the effects of Kraft lignin and Sasobit on the volumetric and mass properties of asphalt mixtures. This included a detailed evaluation of different parameters such as air voids (V_a), binder absorption (P_{ba}), voids in mineral aggregate

(VMA), voids filled with binder (VFA), and density (G_{mm}). The research also focused on evaluating the compatibility and compaction behavior of modified asphalt mixes using the Superpave Gyratory Compactor (SGC) at different gyration levels.

2.4.3.2 Methodology

To achieve the stated objectives, a comprehensive experimental framework was established. This methodology involved the sample preparation and testing of asphalt mixes to evaluate the influence of Kraft lignin and Sasobit on construction temperatures, volumetric and mass properties, and compactability.

Four distinct types of asphalt mixes were prepared to examine the effects of Kraft lignin and Sasobit. The compositions of the materials used in each mix included a reference HMA with no Kraft lignin or Sasobit, HMA modified with 20 % Kraft lignin, WMA with 3 % Sasobit, and WMA with 20 % Kraft lignin and 3 % Sasobit. For each mix, a mix design was developed, and calculations were performed based on the specific conditions of the materials involved.

The SGC was utilized not only to prepare the samples but also to simulate the compaction process, enabling the evaluation of compaction performance. By employing the SGC, the compaction behavior of the asphalt mixtures was examined to assess the effects of Kraft lignin, Sasobit, and their combination on compactability. The determination of mixing and compaction temperatures for each mix was conducted by measuring the viscosity of the binders and applying the constant air void on the SGC samples. Additionally, Compaction was performed at different gyrations to evaluate compaction behavior at different stages, providing a comprehensive understanding of the compaction process for each mix. Furthermore, a comprehensive analysis of key volumetric and mass properties was conducted to evaluate the fundamental characteristics of the asphalt mixes. This analysis involved calculating various parameters.

This third phase of the research established a systematic approach to evaluate the effects of Kraft lignin and Sasobit on asphalt mix properties. By integrating laboratory testing, volumetric and mass analysis, and construction temperature assessments, the study provided comprehensive insights into how these additives influence asphalt mix properties. The findings of this phase were collected and submitted as a research paper titled *"Laboratory Study on the Effect of Kraft Lignin on Construction Temperatures and Physical Properties of Hot and Warm Mix Asphalt Using Sasobit® Additive"* which is currently under review in the Journal of Construction and Building Materials.

2.5 Summary and Contributions

This chapter has outlined the evolution of the research objectives, starting with Aluminosilicate additive and transitioning to Kraft lignin as sustainable asphalt modifier. The experimental framework, structured into three phases, systematically addressed the chemo-thermal, rheological, and physical properties of modified bitumen and asphalt mixtures. Each phase contributed unique insights, advancing the understanding of Kraft lignin and Sasobit as sustainable additives for asphalt production. The subsequent chapters present detailed findings and analyses from these research phases, culminating in recommendations for practical applications and future research directions.

CHAPTER 3

A PRELIMINARY EVALUATION OF ALUMINOSILICATE AS AN ADDITIVE IN WARM MIX ASPHALT: CHALLENGES AND RESULTS

3.1 Introduction

The asphalt industry plays a crucial role in modern infrastructure, with large quantities of asphalt mixtures produced globally each year to meet the demands of road construction and maintenance. This extensive production not only demonstrates the importance of the industry but also creates opportunities for innovation. As sustainability becomes an essential focus, industries generating by-products from different processes are investigating their potential integration into asphalt production. This synergy not only addresses the growing need for efficient waste management but also aligns with the asphalt industry's ongoing efforts to adopt environmentally friendly practices.

In light of this potential intersection of sustainability and innovation, an experimental study was initiated to evaluate the use of Aluminosilicate, a specific type of zeolite, as an additive in asphalt mixtures. Aluminosilicate, supplied as a solid by-product of lithium hydroxide and lithium carbonate production from Spodumene ore by Corporation Nemaska Lithium Inc. in Canada, provided an opportunity for innovation in WMA applications. Previous studies have highlighted the potential of zeolites to induce asphalt foaming, which lowers the viscosity of the asphalt binder, thereby enabling production and compaction at temperatures 20 to 40 °C lower than HMA. This temperature reduction offers significant advantages, including reduced energy consumption and emissions. However, due to variations in the composition and properties of different zeolite types, their performance in asphalt mixtures may vary.

The study aimed to identify the potential and optimal percentage of Aluminosilicate that could achieve the lowest feasible production and compaction temperatures while maintaining or enhancing the functional performance of asphalt mixtures. Additionally, the impact of Aluminosilicate as a filler in asphalt mixtures could be evaluated through comprehensive mechanical testing. The outcomes of WMA incorporating Aluminosilicate were compared with those of conventional HMA, with the expectation that Aluminosilicate could lower production temperatures by up to 40 °C without compromising the performance of the asphalt mixtures.

3.2 Background

Among the various methods employed in WMA, foaming technology stands out as a practical and efficient approach. This technique involves reducing the viscosity of the asphalt binder by creating foaming, which is achieved through the introduction of water into the hot asphalt mix. When the water contacts the hot mix, it rapidly converts to steam, expanding the mix and increasing its specific surface area. This results in improved coating of aggregates and enhanced compaction in the field. The steam eventually evaporates, allowing the asphalt mix to regain its original properties after compaction (Rubio et al., 2012).

Foaming technology can be implemented using two primary techniques: water-based technologies and water-containing materials. The water-based technique involves injecting water (2–4 % of the asphalt mass) directly into the mix using a nozzle, requiring modifications to the asphalt plant. While effective in reducing temperatures by 20–40 °C, the amount of water must be carefully controlled to prevent the separation of aggregates and binder. In addition, water-containing materials such as zeolites offer a practical solution. These materials have crystalline structures that trap water, releasing it gradually when heated to approximately 100 °C. This gradual release enhances workability and reduces production temperatures by approximately 30 °C. Synthetic zeolites such as Advera® and Asphamin® are commonly used in WMA, along with natural zeolites and other water-containing materials (Rubio et al., 2012; Zaumanis, 2014).

Zeolites, also known as crystalline Aluminosilicates, have unique three-dimensional frameworks characterized by uniformly sized pores of molecular dimensions. Their general formula, $Mx/m[(AlO_2)x(SiO_2)y]\cdot H_2O$, describes a structure comprising Silicon, Aluminum, and Oxygen atoms forming interconnected tetrahedrons (Figure 3.1).

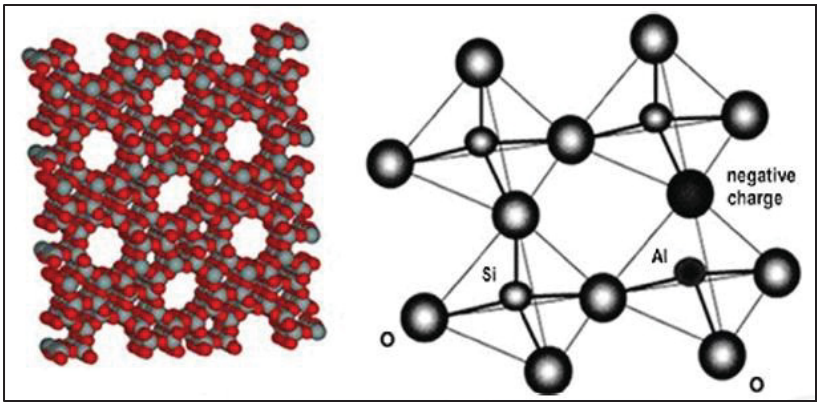


Figure 3.1 Tetrahedrons structure of a typical zeolite

The size and distribution of these pores, ranging from 3 to 30 Å, define the type and functionality of the zeolite. These structural features, combined with a high surface area and ion-exchange capabilities, make zeolites highly useful in various industries, including environmental protection, agriculture, petrochemistry, and construction materials, as shown in Table 3.1 (Cejka, van Bekkum, Corma, & Schueth, 2007).

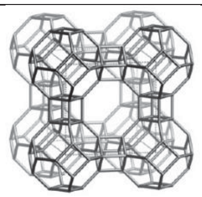
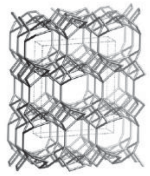
Table 3.1 Zeolite applications in different industries (Król, 2020)

Environmental Protection	Heavy metal sorption
	Water decontamination
	Flue gas treatment
Agriculture	Odour absorber
	Fertilizer additive
	Feed additive
	Aquaculture
Health and hygiene	Pharmaceuticals
	Cosmetics production
	Detergent additive
Petrochemistry	Heterogeneous catalysis
	Purification of gases
	Extraction of petroleum products
Water absorbent	Desiccant
	Heat storage
Active filler	Construction materials
	Paper
	Polymers

In the asphalt industry, zeolites play a critical role as additives in WMA technology. Their ability to release water at elevated temperatures enables the foaming process, which reduces viscosity and enhances the compactability of the mix. Zeolites are categorized as either natural or synthetic. Natural zeolites, such as clinoptilolite and phillipsite, are mined directly, whereas synthetic zeolites, including those derived from fly ash, are produced under controlled hydrothermal conditions. Synthetic products, such as Advera® and Asphamin®, are widely used due to their consistent properties and reliable performance (Sillanpää, 2014; Woszuk & Franus, 2017). The unique properties of zeolites, including their chemical composition, crystalline structure, and pore size, influence their effectiveness as WMA additives. Table 3.2

illustrates the characteristics of three typical zeolites used in WMA, highlighting their framework type, chemical composition, channel size, and accessible volume. These parameters directly impact the foaming behavior, workability, and overall performance of the asphalt mix.

Table 3.2 The crystalline structure and the properties of three types of zeolites used in WMA (Woszuk & Franus, 2016)

Framework type	LTA (Linde A)	GIS (NaP1)	HEU (clinoptilolite)
Zeolite type	Synthetic Zeolite	Synthetic Zeolite	Natural Zeolite
Framework viewed			
Chemical composition	$Na_{96}[Si_{96}Al_{96}O_{384}].$ $216H_2O$	$Na_6[Si_{10}Al_6O_{32}].$ $12H_2O$	$Na_{1.84}K_{1.76}Mg_{0.20}Ca_{1.24}$ $[Si_{29.84}Al_{6.16}O_{72}].$ $21.36H_2O$
Channel size	(8) 4.1 x 4.1 Å	(8) 3.1 x 4.5 Å- (8) 2.8 x 4.8 Å	(10) 3.1 x 7.5 Å + (8) 3.6 x 4.6 Å- (8) 2.8x 4.7 Å
Accessible volume	21.43 % (362.92 Å^3)	9.38 % (91.5 Å^3)	9.42 % (193.53 Å^3)

In conclusion, the integration of zeolites in WMA technology represents a combination of engineering innovation and environmental sustainability.

3.3 Experimental Plan

The experimental plan for this research was designed to comprehensively investigate the potential of Aluminosilicate as an additive in Warm Mix Asphalt (WMA). The study was divided into four key Phases to ensure a comprehensive evaluation of Aluminosilicate's properties, effects, and performance in asphalt mixtures. The following steps outline the methodology:

The first phase focused on characterizing the Aluminosilicate and determining its optimal dosage for reducing the production and compaction temperatures of the asphalt mix. Comprehensive tests were planned to analyze the material's physical and chemical properties, including its water retention capabilities, crystalline structure, and pore size distribution. The goal was to identify the dosage range of Aluminosilicate that minimizes temperature requirements while maintaining workability.

In the second phase, the performance of Aluminosilicate as a filler material in the asphalt mix was planned for evaluation. Aluminosilicate's potential to improve the aggregate-binder interaction and contribute to the mix's overall performance was intended to be analyzed through detailed mechanical and volumetric tests. This step aimed to assess its effect on the density, air voids, and structural stability of the mix.

The third phase involved producing WMA using the optimum Aluminosilicate dosage identified in phase 1. The mechanical properties of the WMA were planned for evaluation through standardized tests, including rutting resistance, tensile strength, and complex modulus tests. These results were compared with those of a control Hot Mix Asphalt (HMA) to determine whether the use of Aluminosilicate provided equivalent or superior performance.

The final phase focused on investigating the ageing characteristics of asphalt mixes incorporating Aluminosilicate. The plan involved extracting the binder from WMA produced with Aluminosilicate and from conventional HMA. The extracted binders were to be subjected to rheological tests, such as the Dynamic Shear Rheometer (DSR) and Bending Beam Rheometer (BBR), and Binder Recovery and Viscosity (BRV). These tests were designed to evaluate the effects of reduced production and compaction temperatures on the rheological properties of the binders.

To initiate this research, the first steps of the initial phase were carried out, focusing on the characterization of Aluminosilicate. The details of these steps are discussed in the following sections.

3.3.1 Materials

The Aluminosilicate used in this study, provided by Corporation Nemaska Lithium Inc. (NMX), is a solid by-product of an innovative process for producing lithium hydroxide and lithium carbonate from Spodumene ore. As shown in Figure 3.2, Aluminosilicate is a fine, white powder commonly classified as a zeolite due to its framework.

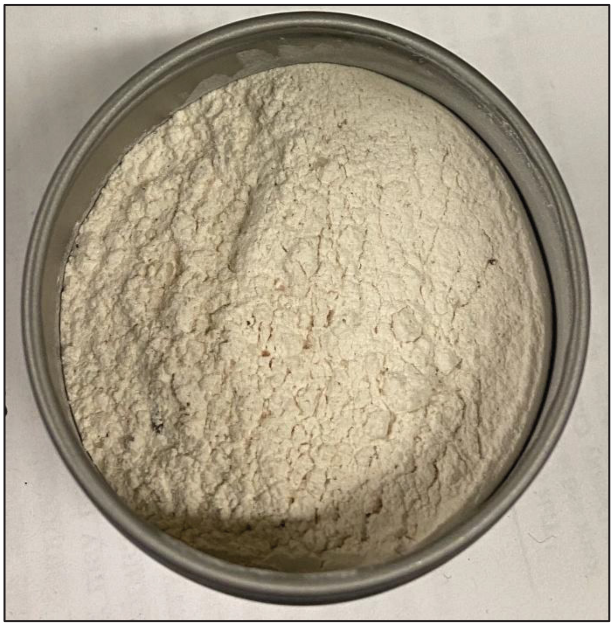


Figure 3.2 Aluminosilicate powder

The detailed chemical composition, including the percentages of all constituent particles as provided by the supplier, is shown in Table 3.3.

Table 3.3 Chemical composition of Aluminosilicate

Particle	%	Particle	%
SiO_2	71.8	MnO	0.06
Al_2O_3	21.2	MgO	0.06
Li_2O	2.41	P_2O_5	0.03
Fe_2O_3	0.69	TiO_2	0.02
Li	0.56	ZrO_2	<0.02
Na_2O	0.43	ZnO	0.01
K_2O	0.32	V_2O_5	<0.01
CaO	0.13	Cr_2O_3	<0.01
S	0.17		

In addition to Aluminosilicate, Limestone filler, which is a fine gray powder commonly used in asphalt mixes, was also included in this study. The limestone filler was selected to serve as a comparative material for evaluating the water content of Aluminosilicate. By comparing the water release characteristics of Aluminosilicate with those of limestone filler, a better understanding of the unique behavior and potential advantages of Aluminosilicate as an additive in WMA could be achieved.

3.3.2 Sample Preparation

For the determination of water content, the original powders of Aluminosilicate and Limestone filler were directly used in the testing process. However, to evaluate the foaming capability of Aluminosilicate through microscopic observations, a specific procedure was designed to prepare and analyze the samples.

Aluminosilicate was added to hot bitumen at concentrations of 1 and 2 % by weight of bitumen. The mixing process was conducted using a mechanical mixer at a temperature of 150 °C, with a mixing duration of 10 minutes. For comparison, one additional sample were prepared using

1 % limestone filler, as well as a control sample of virgin bitumen without any additives. After mixing, all samples were immediately placed in a freezer for one day to preserve the probably trapped bubbles generated by the foaming effect. Freezing ensured that the microstructural changes resulting from the foaming process were stabilized for further analysis. Following the freezing step, the samples were carefully broken to expose the internal structure, allowing for microscopic imaging. The steps involved in sample preparation and analysis are illustrated in Figure 3.3.

Figure 3.3 Sample Preparation Process for microscopic observations: (a) Mixing bitumen with Aluminosilicate and filler, (b) Mixed samples in the mold, (c) Samples placed in the freezer, (d) Breaking the frozen samples and ready for microscopic observations

3.3.3 Testing

3.3.3.1 Determination of water content

The water content of Aluminosilicate was determined following the guidelines outlined in ASTM D2216 which is “Standard test methods for laboratory determination of water (moisture) content of soil and rock by mass”. This standard provides a reliable method for measuring the moisture content of materials by determining the mass of water present relative to the dry mass of the sample.

To begin, a representative sample of Aluminosilicate and Limestone filler was obtained and homogenized to ensure consistency. The initial mass of the sample was measured using a high-precision balance to record its wet weight in its natural or as-received state (Figure 3.4).

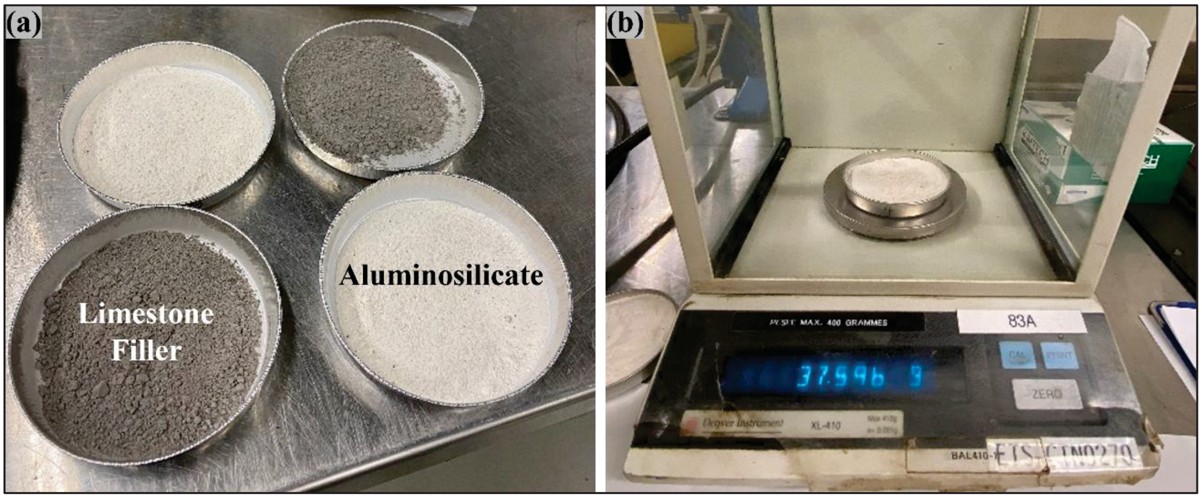


Figure 3.4 Preparation (a) and Measurement (b) of Aluminosilicate and Limestone filler Samples for Water Content Testing

The sample was then placed in a conventional drying oven without a fan to prevent the loss of powders and unintended weight reduction during the drying process. The oven was set to a controlled temperature range, starting from 80 °C and increasing incrementally to 160 °C, with the sample kept at each temperature for one hour to allow measuring water present in the sample. To ensure precise control of the testing temperature, a thermometer was used and continuously monitored throughout the testing procedure. After drying, the sample was cooled to room temperature and stored overnight in a desiccator to prevent moisture reabsorption. Its dry mass was then recorded. The water content was calculated using the following Equation 3.1:

$$\text{Water Content (\%)} = \left(\frac{\text{Wet Sample Mass} - \text{Dry Sample Mass}}{\text{Dry Sample Mass}}\right) \times 100 \qquad \text{Equation 3.1}$$

This procedure was repeated for various temperature points including 80, 90, 100, 110, and up to 160 °C to analyze the water release characteristics of Aluminosilicate across a range of temperatures. The same procedure was applied to Limestone filler used in asphalt mixtures for comparison. Figure 3.5 shows the experimental setup, including the oven used for drying samples and the thermometer for monitoring temperature accuracy. The detailed and standardized approach ensures accurate and reproducible results, providing essential insights into the water release behavior of Aluminosilicate. These findings are critical for understanding its performance as an additive in WMA.

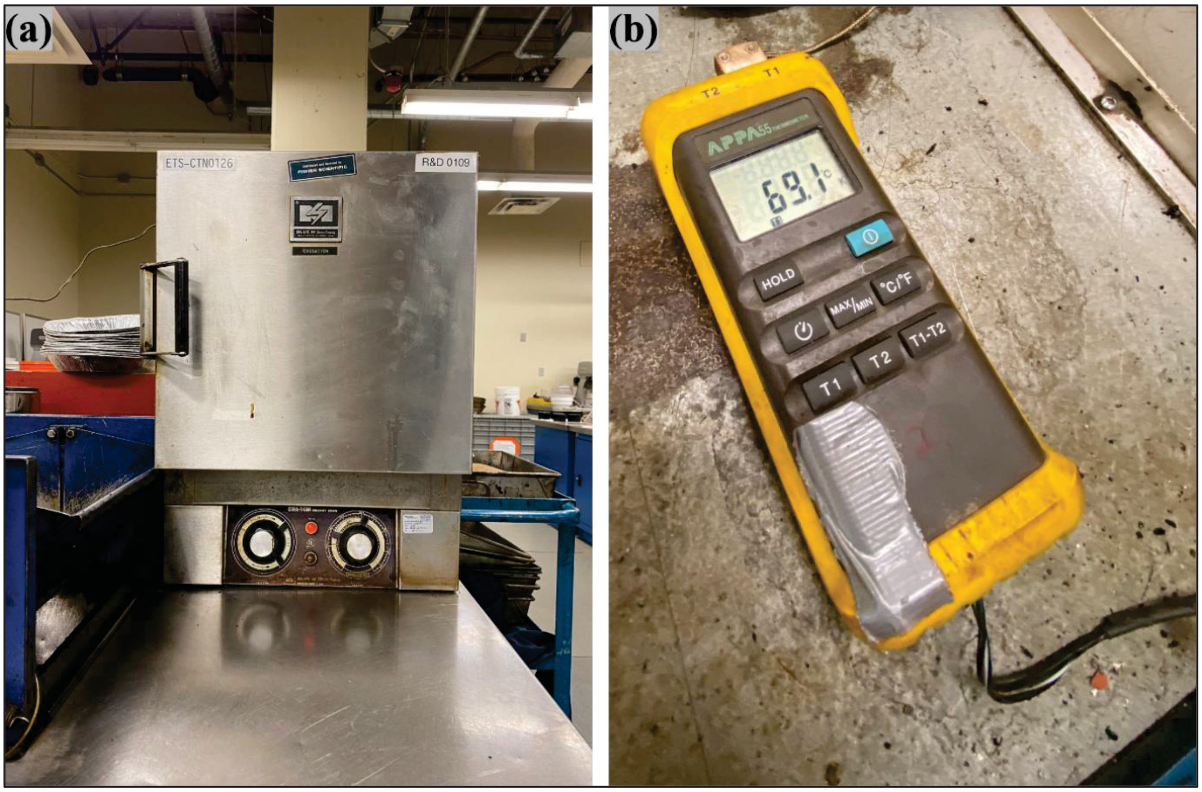


Figure 3.5 Experimental Setup for Water Content Determination including (a) conventional oven and (b) Thermometer

3.3.3.2 Microscopic Observations

Microscopic analysis of the Aluminosilicate samples was conducted using the ZEISS SteREO Discovery.V8 microscope, as shown in Figure 3.6. This instrument features an 8:1 zoom ratio, providing magnifications from 1x to 8x, which facilitates a detailed examination of sample morphology. The microscope's modular design allows for the integration of various illumination techniques, such as brightfield and darkfield, enabling comprehensive analysis of the sample's surface characteristics. These capabilities were instrumental in accurately assessing the physical properties of the Aluminosilicate additive, thereby informing its potential efficacy in WMA applications.

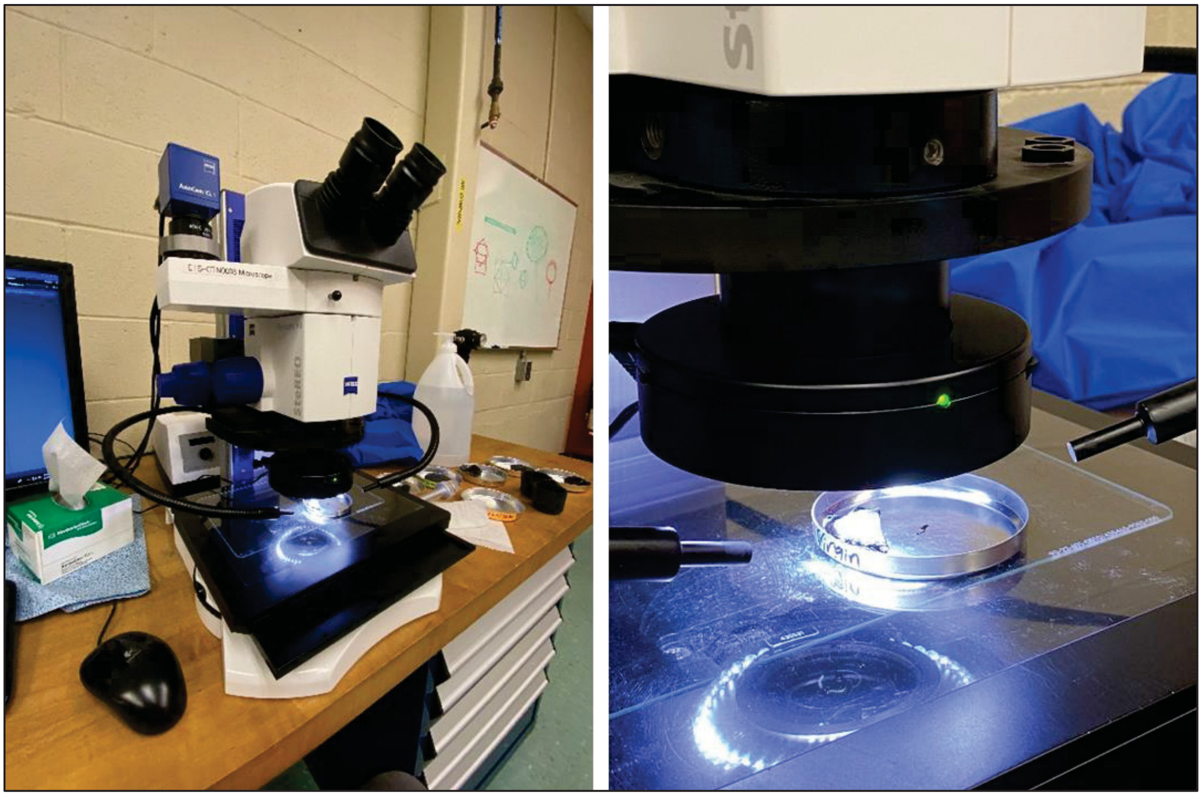


Figure 3.6 Microscope setup for microscopic observation of samples

3.4 Test Results and Discussion

3.4.1 Water Content test results and Analysis

The water content test results of Aluminosilicate and Limestone filler are shown in Figure 3.7. The results show that Aluminosilicate consistently exhibited higher water content than limestone filler across the entire temperature range. However, the difference in water content between the two materials is not significant. At 80 °C, the water content of Aluminosilicate was measured at 0.27 %, while that of the limestone filler was 0.21 %. This trend continued at 90 °C, with Aluminosilicate maintaining a slight increase in water content at 0.24 % compared to 0.18 % for Limestone filler. A slight increase in the water content of Aluminosilicate was observed at 100 °C, where it reached 0.35 %. This increase is indicative of the release of moisture, likely from the material's porous structure. Beyond 100 °C, the water content of Aluminosilicate stabilized, remaining consistent at approximately 0.35 %. Meanwhile, the Limestone filler exhibited the same trend in water content variation. However, the water content of limestone filler was consistently lower than that of Aluminosilicate throughout the tests.

Despite the differences observed, the overall water content of both materials remained minimal. The water release observed in Aluminosilicate, while slightly higher than that of the limestone filler, was significantly lower than the crystalline water content reported for zeolites commonly used in WMA. This limited water content suggests that the Aluminosilicate tested in this study lacks sufficient crystalline water to produce a meaningful foaming effect in bitumen. As such, its performance in WMA applications, particularly in reducing production and compaction temperatures through foaming, is likely to be limited.

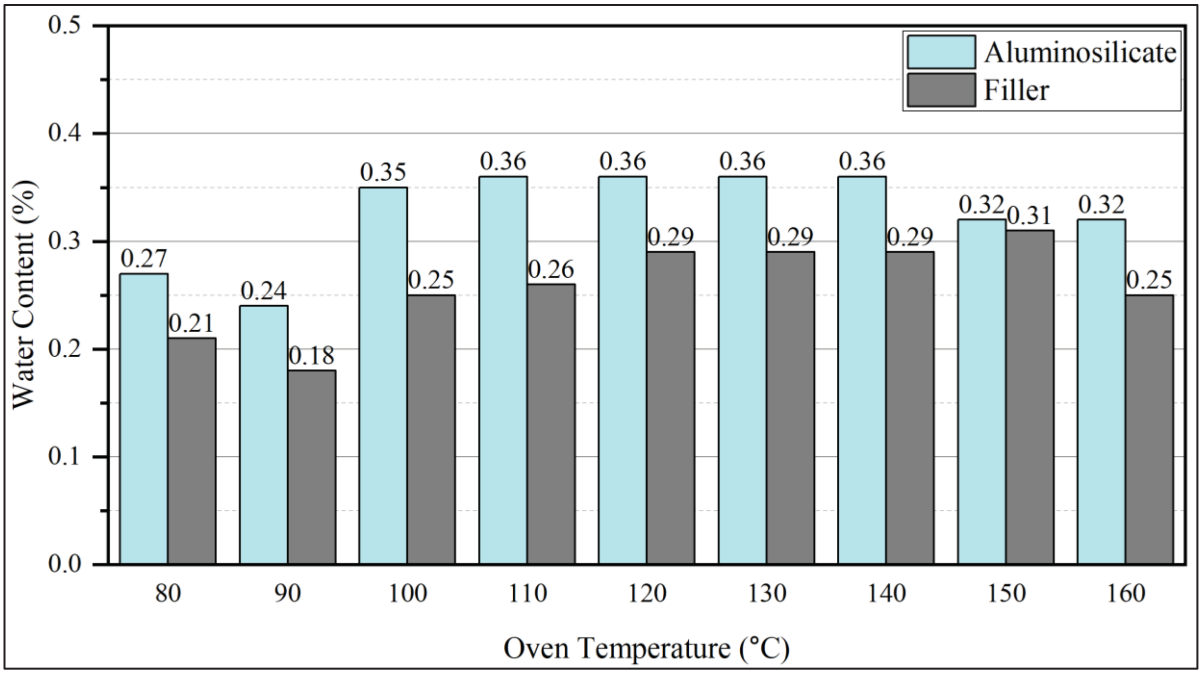


Figure 3.7 Water content of Aluminosilicate and Limestone filler at various oven temperatures

3.4.2 Microscopic Observations and Analysis

Microscopic observations were conducted to evaluate the foaming effect of Aluminosilicate and compare it to virgin bitumen and bitumen mixed with filler. The images shown in Figure 3.8 correspond to (a) virgin bitumen, (b) Bitumen with 1 % Filler, (c) Bitumen with 1 % Aluminosilicate, (d) Bitumen with 2 % Aluminosilicate. These observations aimed to assess the presence and density of bubbles formed within the bitumen matrix, a key indicator of foaming performance in WMA.

The first image (a) of virgin bitumen reveals a uniformly dark and bubble-free structure, as expected for unmodified asphalt binder. In the image (b), representing bitumen mixed with 1 % filler, minimal changes are observed, with the structure remaining nearly bubble-free. This suggests that the addition of filler does not contribute to any noticeable foaming effect.

In image (c), corresponding to 1 % Aluminosilicate, an increase in the number of microbubbles is evident. The presence of these bubbles indicates that the addition of Aluminosilicate has a slight effect on the bitumen structure. However, the density of bubbles remains relatively low. Image (d), representing 2 % Aluminosilicate, shows a further increase in both the number and density of bubbles compared to 1 % Aluminosilicate. This increase may be attributed to the release of moisture from the Aluminosilicate structure during mixing. Despite this improvement, the overall bubble density remains significantly lower than what is typically required to achieve a substantial foaming effect in WMA.

The results suggest that while the addition of Aluminosilicate produces some foaming, the effect is insufficient to meet the expectations for WMA technology. In WMA, a higher density of bubbles is critical to reduce the viscosity of the asphalt binder effectively and enable production and compaction at lower temperatures. The low bubble formation observed in this study indicates that the Aluminosilicate tested may not possess the necessary characteristics, such as adequate water release, to serve as an effective foaming agent for WMA applications.

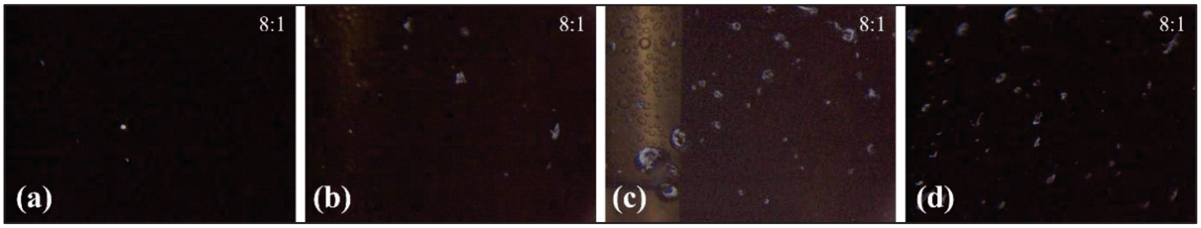


Figure 3.8 Microscopic Observations at 8:1 optical zoom: (a) Virgin Bitumen, (b) Bitumen with 1 % Filler, (c) Bitumen with 1 % Aluminosilicate, (d) Bitumen with 2 % Aluminosilicate

3.5 Conclusion

The findings from the water content tests and microscopic observations collectively suggest that the Aluminosilicate tested in this study is unlikely to serve as an effective additive for WMA. The water content analysis revealed that the water present in Aluminosilicate was significantly lower than the levels typically required to achieve a meaningful foaming effect.

While the microscopic observations demonstrated a slight increase in microbubble formation with the addition of Aluminosilicate, the overall density and distribution of bubbles remained insufficient to reduce the viscosity of the asphalt binder and meet the performance expectations of WMA technology.

Given these limitations, the decision was made to discontinue the Aluminosilicate project and shift the focus to an alternative research direction involving lignin as a bio additive in asphalt mixtures. While the Aluminosilicate project did not progress further, it provided valuable insights into the material's properties and its limitations for asphalt applications, which can inform future studies in the field.

CHAPTER 4

PARTICLE SIZE DISTRIBUTION OF DIFFERENT TYPES OF LIGNIN

4.1 Introduction

This chapter explores the particle size distribution (PSD)characteristics of multiple lignin types supplied by FPInnovations. These types include acid-form and base-form lignin samples from different sources, each with unique solubility and granulometric properties. The analysis focuses on the influence of source of lignin, preparation techniques, such as grinding and solvent dispersion, on the PSD of these lignin samples.

The results presented in this chapter highlight the PSD variations between different lignin forms and treatments, emphasizing the role of lignin type, processing conditions, and solvent medium. These insights contribute to a deeper understanding of the material's behavior, paving the way for its effective utilization in sustainable asphalt applications and beyond.

4.2 Background

PSD is a fundamental parameter in the characterization of granular materials, including powders and natural polymers such as lignin. PSD significantly affects the physical, chemical, and mechanical properties of materials, which has implications for their performance in various industrial applications. In the context of lignin, a complex biopolymer derived from biomass, PSD plays a crucial role in determining its behavior as a binder modifier in asphalt mixtures and other composite materials. Understanding the PSD of different types of lignin is essential to optimize its dissolution behavior, reactivity, and compatibility with other materials. This section provides a comprehensive overview of PSD, covering its definition, measurement techniques, key parameters, and its relevance to lignin processing and applications.

4.2.1 Definition and Significance of Particle Size Distribution

Particle Size Distribution (PSD) refers to the statistical distribution of particle sizes within a given sample. It indicates the proportion or percentage of particles within specific size ranges, providing insight into particle homogeneity and overall material behavior. PSD is typically presented in two forms; 1) Differential PSD, which displays the frequency or volume of particles within each size range, and 2) Cumulative PSD, which represents the percentage of particles smaller than a particular size (Goliszek et al., 2018).

These distributions are often presented graphically as histograms or cumulative curves, enabling the visualization of particle size variability. The PSD influences crucial material properties such as flowability, solubility, reactivity, and mechanical performance. For instance, in the asphalt industry, finer particles with narrow PSDs facilitate better dispersion and enhance the adhesion between binder and aggregate, leading to improved mechanical performance (Makkonen, 2024).

4.2.2 Measurement Techniques for PSD

Various methods are used to measure PSD, with the choice of technique depending on the particle size range, material type, and precision required. The most common PSD measurement techniques include:

4.2.2.1 Laser Diffraction

Laser Diffraction is one of the most widely used methods for PSD analysis due to its speed, accuracy, and ability to measure particles ranging from nanometers to millimeters. It works by measuring the angular variation of light scattered by particles as they pass through a laser beam (Figure 4.1). The particle size is calculated by comparing the measured scattering pattern to theoretical models, typically the Mie theory. The accuracy of laser diffraction depends on the refractive index of both the particle and the dispersion medium (de Carvalho et al., 2015).

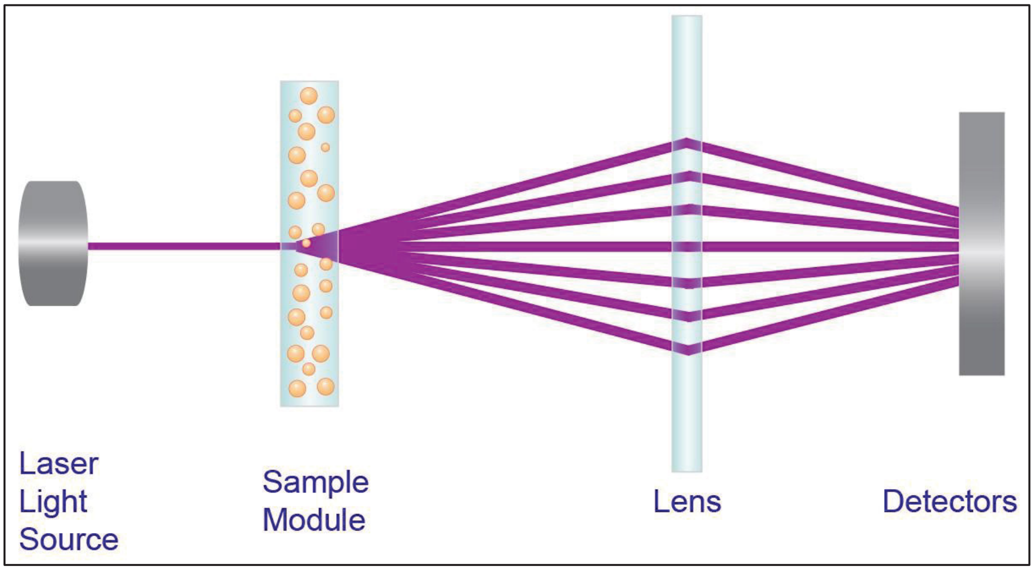


Figure 4.1 Principle of Laser Diffraction for Particle Size Analysis
Taken from Ullah et al. (2022)

4.2.2.2 Dynamic Light Scattering (DLS)

DLS technique is commonly used for smaller particles, especially nanoparticles. As shown in Figure 4.2, it measures the fluctuations in scattered light caused by Brownian motion of particles in a suspension, providing the hydrodynamic diameter of the particles. DLS is particularly useful for colloidal systems but assumes spherical particles, which may introduce errors for non-spherical lignin particles (Yadav, Saini, & Maji, 2017).

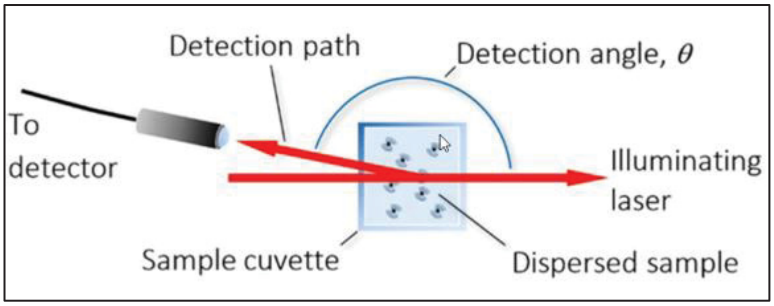


Figure 4.2 Schematic illustration of Dynamic Light Scattering (DLS) Measurement Principle for Particle Size Distribution Analysis

Taken from Malm & Corbett (2019)

4.2.2.3 Sieve Analysis

Sieve Analysis is a simple, low-cost method for measuring particle sizes in larger, coarser particles. It involves passing the sample through a series of sieves with decreasing mesh sizes, as illustrated in Figure 4.3. Although simple, this method is limited to particle sizes larger than approximately 20 microns and is less precise than laser diffraction and DLS (de Carvalho et al., 2015).

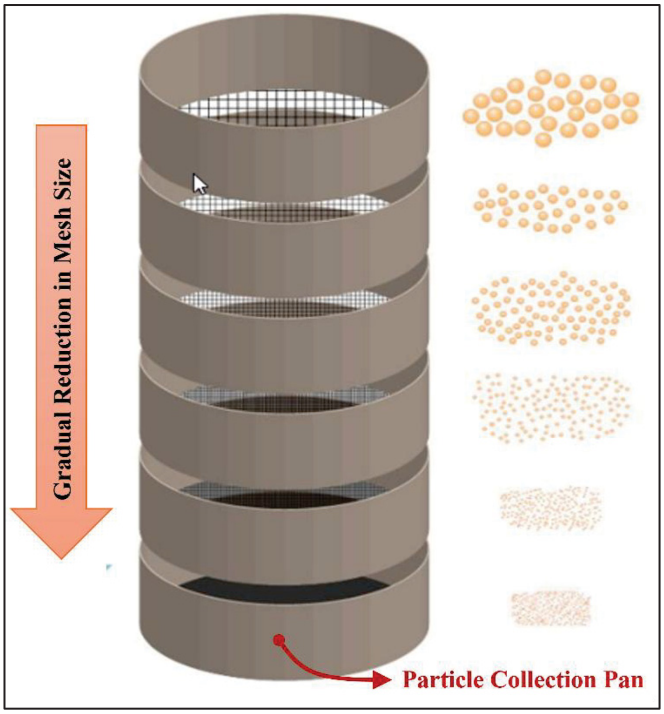


Figure 4.3 Illustration of Sieve Analysis Method for Particle Size Distribution Determination Taken from ParticleTechnologyLabs website (2025)

4.2.2.4 Image Analysis

Image Analysis method uses high-resolution images to analyze particle sizes and shapes. It provides information on particle morphology, which is useful for non-spherical particles such as lignin. Advanced image analysis can measure the Feret diameter, aspect ratio, and other shape-related parameters (Souza & Menegalli, 2011).

Each method has its limitations. For instance, laser diffraction assumes spherical particles, which may not be accurate for irregularly shaped particles like lignin. Similarly, DLS is sensitive to particle shape and often provides an average hydrodynamic diameter that may not reflect the actual particle size distribution.

4.2.3 Key Parameters in PSD Analysis

PSD is typically characterized using statistical parameters that describe the central tendency, spread, and width of particle sizes. The most relevant parameters are:

4.2.3.1 D10, D50, and D90

These are percentile-based size descriptors. D10 represents the size (particle diameter) at which 10 % of the sample's mass is smaller. D50 corresponds to the size below which 50 % of the particles lie, also known as the median particle size. D90 indicates the size below which 90 % of the particles lie (Figure 4.4). These values are useful for understanding the spread of particle sizes within a sample and are widely used in the analysis of lignin PSD.

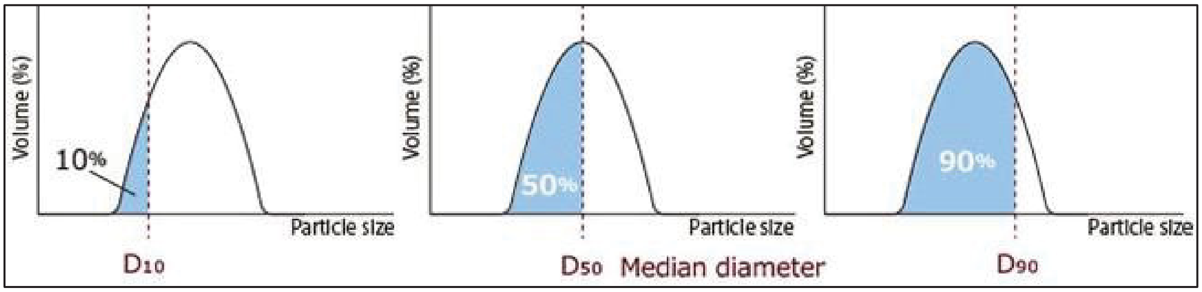


Figure 4.4 Graphical Representation of D10, D50, and D90 for PSD Analysis
Taken from ThinkyLibrary website (2025)

4.2.3.2 Mean, Median, and Mode:

The mean is the arithmetic average of particle sizes. The median (D50) is the value at which 50 % of the particles are smaller and 50 % are larger. The mode represents the most frequently occurring particle size in the distribution. For symmetric distributions, these values are equal, but for skewed distributions, the median is often used as a more robust indicator of particle size.

4.2.3.3 Span

This is a measure of distribution width and is calculated as shown in Equation 4.1:

$$Span = \frac{D90 - D10}{D50} \qquad \text{Equation 4.1}$$

A smaller span indicates a more uniform particle size distribution, which is beneficial in applications where particle uniformity is essential, such as in asphalt binders.

4.2.3.4 Full Width at Half Maximum (FWHM)

The FWHM parameter measures the width of the distribution at half the peak height and is often used for unimodal distributions.

4.2.3.5 Skewness

Skewness parameter identifies the symmetry of the distribution curve. A positively skewed curve has a longer tail to the right, while a negatively skewed curve has a longer tail to the left (Gee & Or, 2002).

4.2.4 Role of PSD in Lignin Behavior and Applications

Lignin is a complex, heterogeneous biopolymer with diverse structural characteristics depending on its source (e.g., softwood or hardwood) and the method of extraction (e.g., Kraft, soda, or organosolv lignin). The PSD of lignin influences its behavior in suspension, its dissolution in solvents, and its role as a binder modifier in asphalt mixtures.

- **Flowability:** Lignin powders with smaller PSDs exhibit improved flowability, which enhances processability during blending and mixing in asphalt binders. The reduced interparticle friction in powders with uniform particle sizes contributes to better material handling (Österberg, Sipponen, Mattos, & Rojas, 2020).

- **Solubility:** The PSD of lignin affects its dissolution in aqueous or solvent-based systems. Smaller particles have a higher surface area, facilitating faster dissolution. This property is especially relevant for lignin applications in adhesives and coatings, where efficient dissolution is required (Vainio et al., 2004).
- **Reactivity:** The particle size of lignin affects the exposure of reactive functional groups, influencing its reactivity during chemical modification. Finer particles provide better access to reactive sites, enhancing chemical reactions in processes such as depolymerization (Tolkachev, Koklin, Laptinskaya, Lunin, & Bogdan, 2019).

4.2.5 Relevance of PSD in Lignin's Role in Asphalt Modification

In asphalt modification, the PSD of lignin is a key factor that influences the homogeneity, mechanical performance, and durability of asphalt mixtures. Research has shown that lignin with finer particle sizes provides better dispersion in asphalt binders, reducing the likelihood of particle agglomeration. This enhances the compatibility of lignin with bitumen, ensuring uniform modification and improved mechanical properties of the final product (Maršík et al., 2024).

Studies suggest that lignin particles in the nanoscale range exhibit better performance in asphalt mixtures. Finer particles have a larger surface area, leading to enhanced interaction with the asphalt matrix. The ability to control the PSD of lignin through grinding, sieving, and solvent dispersion allows for the customization of lignin-based asphalt modifiers to meet specific performance requirements (Beisl, Miltner, & Friedl, 2017; Österberg et al., 2020).

4.3 Experimental Plan

4.3.1 Materials

This study utilized sixteen (16) lignin samples provided by FPInnovations to evaluate their PSD. The samples were sourced from three distinct locations in Canada, namely Hinton, Kruger, and Thunder Bay, and represent two wood types, softwood and hardwood. In addition to these samples, Kraft lignin, the provider's main product, was also included. This type of lignin, given its prominence and availability, was the primary focus of the project.

Softwood, derived from coniferous trees like pine and spruce, is typically less dense and grows faster than hardwood, which comes from deciduous trees such as oak and maple. These inherent differences influence the physical properties and potential applications of the wood. The lignin samples were classified by potential of hydrogen (pH) into acid-form lignins, characterized by a pH less than 7, and base-form lignins, with a pH greater than 7. This classification is crucial for understanding how chemical composition affects the physical and dispersive properties of lignin during particle size distribution analysis.

These lignin samples were processed in various procedures. The processing included grinding to break down the clumpy mass into smaller particles, which was done once (1st Grinded) or twice (2nd Grinded). Additionally, some samples underwent sieving to achieve specific particle size distributions. The modified versions of the lignin samples were subjected to an additional process referred to as “modified” by the provider, though the exact details of this modification were not disclosed. Table 4.1 provides a detailed description of each sample.

Table 4.1 Details of Lignin Samples by Source, Wood Type, Form, and Processing Conditions

No.	Sample Names	Source	Wood Type	Form	Process Details
1	Kraft Lignin	Unknown	Softwood	Acid	-
2	HTSWA	Hinton	Softwood	Acid	-
3	HTSWA-Modified	Hinton	Softwood	Acid	Modified
4	HTSWA-60mesh	Hinton	Softwood	Acid	60 mesh
5	HTSWA-100mesh	Hinton	Softwood	Acid	100 mesh
6	KSWA-1	Kruger	Softwood	Acid	1st Grinded
7	KSWA-2	Kruger	Softwood	Acid	2nd Grinded
8	KSWA-Modified	Kruger	Softwood	Acid	Modified
9	TBHWA-1	Thunder Bay	Hardwood	Acid	1st Grinded
10	TBHWA-2	Thunder Bay	Hardwood	Acid	2nd Grinded
11	HTSWB-1	Hinton	Softwood	Base	1st Grinded
12	HTSWB-2	Hinton	Softwood	Base	2nd Grinded
13	KSWB-1	Kruger	Softwood	Base	1st Grinded
14	KSWB-2	Kruger	Softwood	Base	2nd Grinded
15	TBHWB-1	Thunder Bay	Hardwood	Base	1st Grinded
16	TBHWB-2	Thunder Bay	Hardwood	Base	2nd Grinded

Figure 4.5, visually illustrates the diversity of lignin samples, highlighting their various textures and colors. This diversity reflects variations due to source, chemical characteristics, and processing methods, underscoring the importance of systematic testing to understand their impact on the granulometric properties of lignin.

Figure 4.5 Lignin Samples Prepared for Particle Size Distribution (PSD) Analysis

4.3.2 Testing

Particle size measurements were conducted using laser granulometry with the Mastersizer 3000, equipped with a Hydro EV dispersion unit. This unit is designed to efficiently disperse samples in liquid media, ensuring precise and reproducible measurements. For the initial phase of the testing, water was used as the dispersion medium to prepare the lignin samples. Given the pH diversity of the lignin samples, isopropanol was also employed as the dispersion medium for some samples to ensure effective particle suspension and compatibility. The particle size distribution was measured across a broad range from 0.01 µm (10 nanometers) to 500 µm. The choice of this range ensures comprehensive characterization of the lignin samples. A stirrer was employed during the dispersion process to achieve a homogenous mixture, reducing the likelihood of particle aggregation. Figure 4.6 illustrates the testing setup in this study.

Figure 4.6 Experimental Setup for Laser Granulometry Test Using Mastersizer 3000

4.4 Test Results and Discussion

4.4.1 Visual Observations and Dispersion Behavior of Lignin Samples

During the initial phase of testing, lignin samples were blended with water to evaluate their solubility. Observations revealed distinct differences between acid-form and base-form lignin samples, emphasizing the critical role of pH in influencing their interaction with water. As shown in Figure 4.7, Acid-Form Lignin Samples are mostly insoluble in water. The lignin particles are clearly visible within the water, forming a suspension rather than dissolving completely. For the laser granulometry test, all lignin particles need to be suspended in the dispersion medium while stirring to ensure accurate measurement of particle sizes through the device's pipes. This condition was achieved for acid-form lignin samples, as the particles remained suspended and visible, making them suitable for particle size distribution analysis in water.

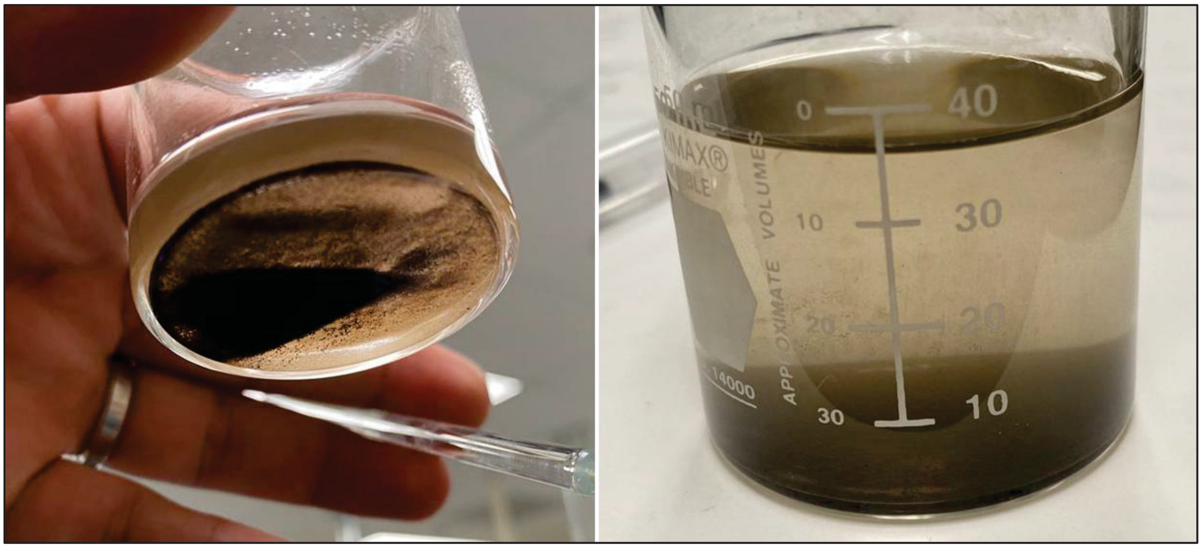


Figure 4.7 Visual Observation of Acid-Form Lignin Samples

In contrast, base-form lignin samples exhibited distinctly different behavior, as illustrated in Figure 4.8. These samples dissolved in water, turning the water into a yellowish color, homogenous solution and making the particles invisible. Since the particles were no longer suspended, it was technically impossible to measure their sizes using water as the dispersion medium. To address this issue, Isopropanol was selected as an alternative dispersion medium. In Isopropanol, the base-form lignin particles remained suspended and visible, enabling them to pass through the device's pipes and ensuring accurate particle size measurements. This distinction between acid-form and base-form lignin behavior has broader implications. It highlights the importance of considering the lignin source and processing steps, which are crucial for determining its feasibility and potential applications in various industries.

Furthermore, these findings could be linked to bitumen applications, where lignin's role might vary. Depending on its potential physical or chemical interaction with the bitumen matrix, lignin may act either as a filler or as a soluble component.

Figure 4.8 Visual Observation of Base-Form Lignin Samples

4.4.2 PSD test results

To gain a comprehensive understanding of the particle size distribution and its correlation with the lignin types, the results were systematically analyzed based on the sources of lignin as well as their classification into acid and base forms. The results are presented as volume density and cumulative volume plotted against particle size. Detailed numerical data for all samples are summarized in Table 4.2, providing a comprehensive overview of their particle size characteristics.

Table 4.2 Particle size distribution results for lignin samples

No.	Group	Lignin samples	D10 (μm)	D50 (μm)	D90 (μm)	Span
1	HTSWA	HTSWA	2.88	10.70	40.80	3.54
2		HTSWA 60mesh	3.05	11.70	41.20	3.26
3		HTSWA 100mesh	3.13	12.50	44.60	3.38
4		HTSWA modified	3.82	16.40	104.00	6.11
5	HTSWB	HTSWB 1st	15.50	55.40	150.00	2.43
6		HTSWB 2nd	10.20	32.30	80.10	2.16
7	KSWA	KSWA 1st	0.03	3.84	47.20	12.28
8		KSWA 2nd	0.03	2.24	30.10	13.42
9		KSWA modified	0.03	3.91	61.60	15.75
10	KSWB	KSWB 1st	-	-	-	-
11		KSWB 2nd	11.30	65.90	162.00	2.87
12	TBHWA	TBHWA 1st	0.03	3.58	17.60	4.91
13		TBHWA 2nd	0.03	3.79	20.80	5.48
14	TBHWB	TBHWB 1st	4.82	35.30	138.00	3.78
15		TBHWB 2nd	5.38	62.40	135.00	2.08

The Kraft lignin sample, which serves as the primary focus of this research project, exhibited a PSD within the range of 1 to 100 μm, as illustrated in Figure 4.9. The analysis revealed that 80 % of the particles were distributed between 5.47 μm (D10) and 48.7 μm (D90), with a median particle size (D50) of 14.3 μm. This relatively narrow size range indicates a high degree of uniformity in particle sizes. The similarity in particle sizes enhances the compatibility of Kraft lignin with bitumen, as uniform particles contribute to homogeneous blending and reduce the likelihood of agglomeration.

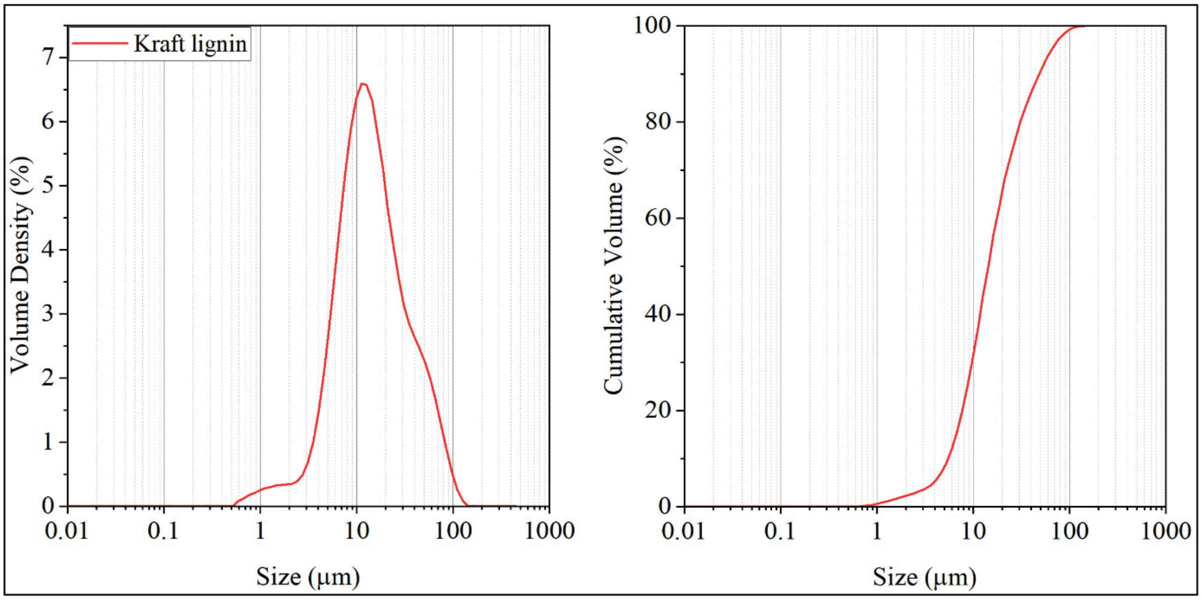


Figure 4.9 Particle size distribution of Kraft lignin sample

According to Figure 4.10, the D50 for the HTSWA, HTSWA-60mesh, and HTSWA-100mesh lignin powders are 10.7, 11.7, and 12.5 μm, respectively, showing almost identical values. The modified HTSWA sample exhibits a slightly larger median particle size of 16.4 μm. This indicates that the modification process caused particle agglomeration or resulted in coarser particle sizes. The broader span value for the modified sample reflects a wider particle size distribution compared to the other samples. As shown in the cumulative particle size distribution diagram, the modified HTSWA sample demonstrates a noticeable rightward shift, further confirming the increase in particle size caused by the modification process. These observations highlight the influence of processing methods, particularly sieving and modification, on the particle size characteristics of HTSWA lignin samples.

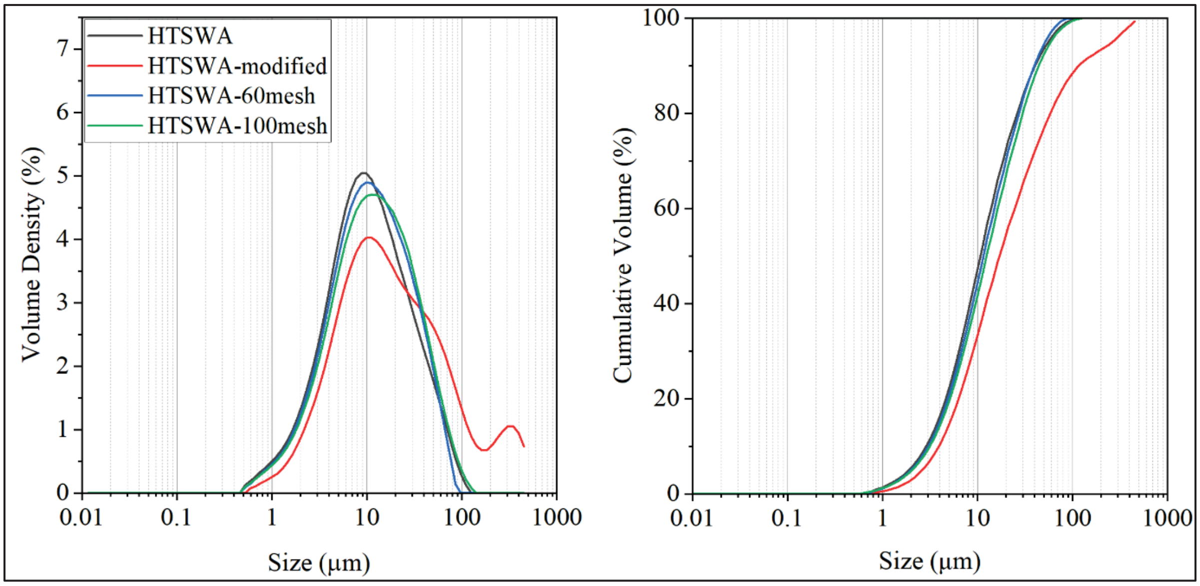


Figure 4.10 Particle size distribution of HTSWA samples

For HTSWB samples, Figure 4.11 shows that the 2nd grinded HTSWB has a slight shift to the left compared to the 1st grinded sample, indicating finer particle sizes. This result is expected, as the additional grinding process reduces particle size further.

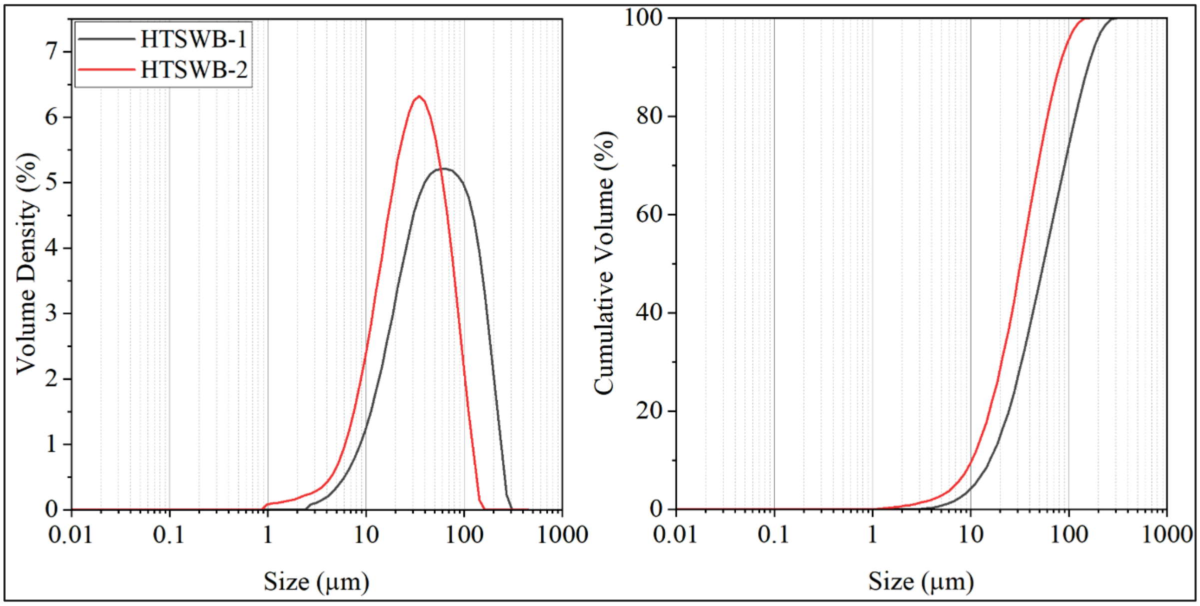


Figure 4.11 Particle size distribution of HTSWB samples

As shown in Figure 4.12, For the acid-form Kruger lignin samples (KSWA), the particle size distribution results indicate minimal variation between the 1st grinded and 2nd grinded samples, suggesting that the additional grinding had a limited impact on overall particle size. However, the modified KSWA sample exhibits a slight increase in D90 compared to the other two, indicating the presence of larger particles and a broader size distribution.

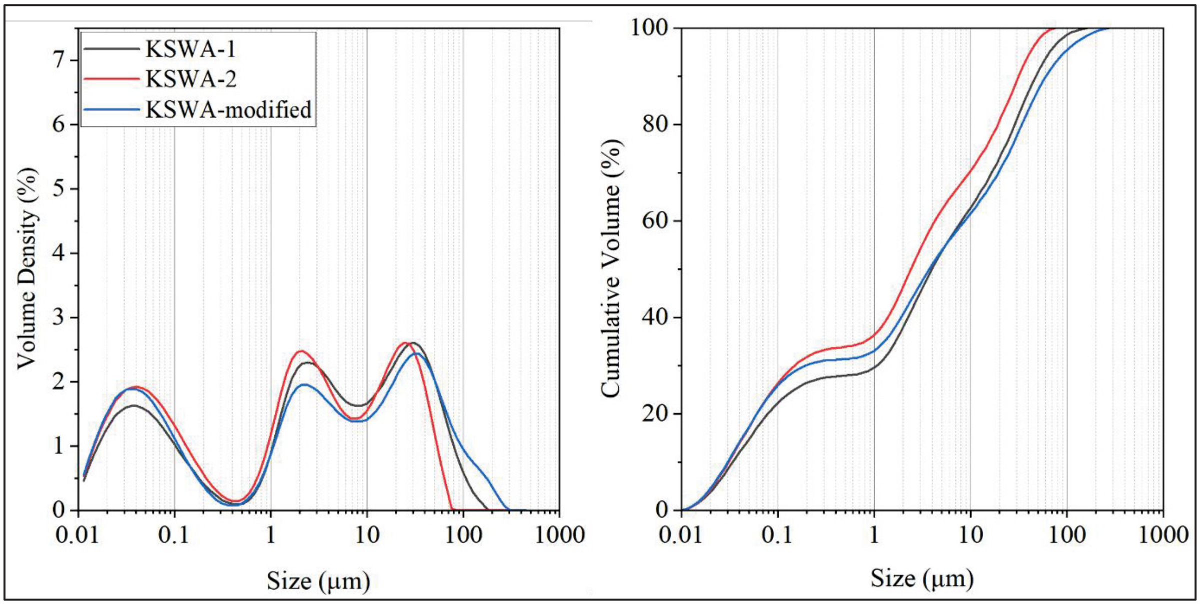


Figure 4.12 Particle size distribution of KSWA samples

For the KSWB samples, the particle size distribution measurement of KSWB 1st was not feasible using this technique due to coarser particles which stuck in the device. However, for the KSWB 2nd sample, as shown in Figure 4.13, the measurement was successfully conducted, demonstrating that the second grinding step effectively reduced particle size and is comparable with other lignin types.

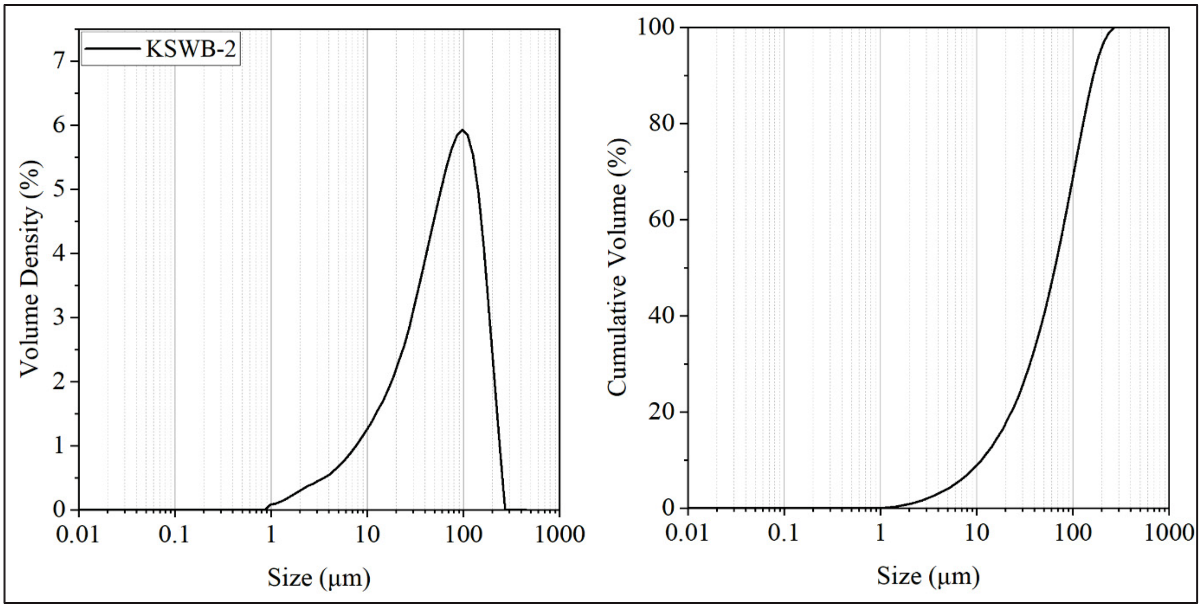


Figure 4.13 Particle size distribution of KSWB sample

For the TBHWA samples, the particle size distribution results, as shown in Figure 4.14, indicate that the PSD is similar for both the 1st grinded and 2nd grinded samples.

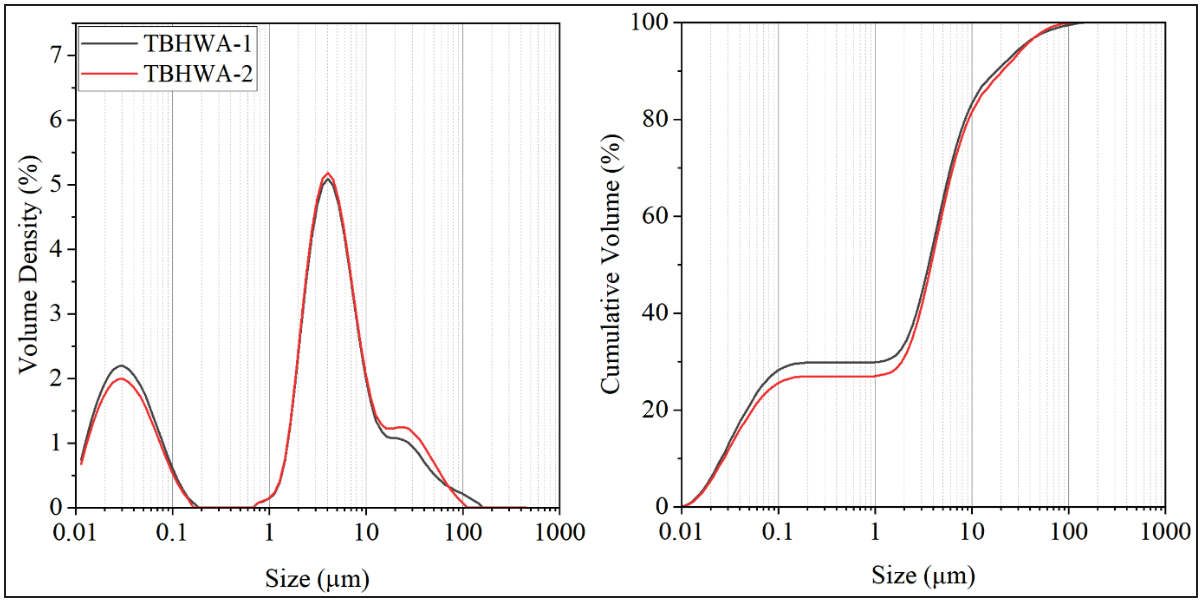


Figure 4.14 Particle size distribution of TBHWA samples

For the TBHWB samples, as shown in Figure 4.15, the particle size distribution reveals noticeable differences between the 1st grinded and 2nd grinded samples. The concentration of particle size in the 2nd grinded sample is around 90 µm, indicating a more uniform particle size distribution. In contrast, the 1st grinded sample exhibits a broader range of particle sizes.

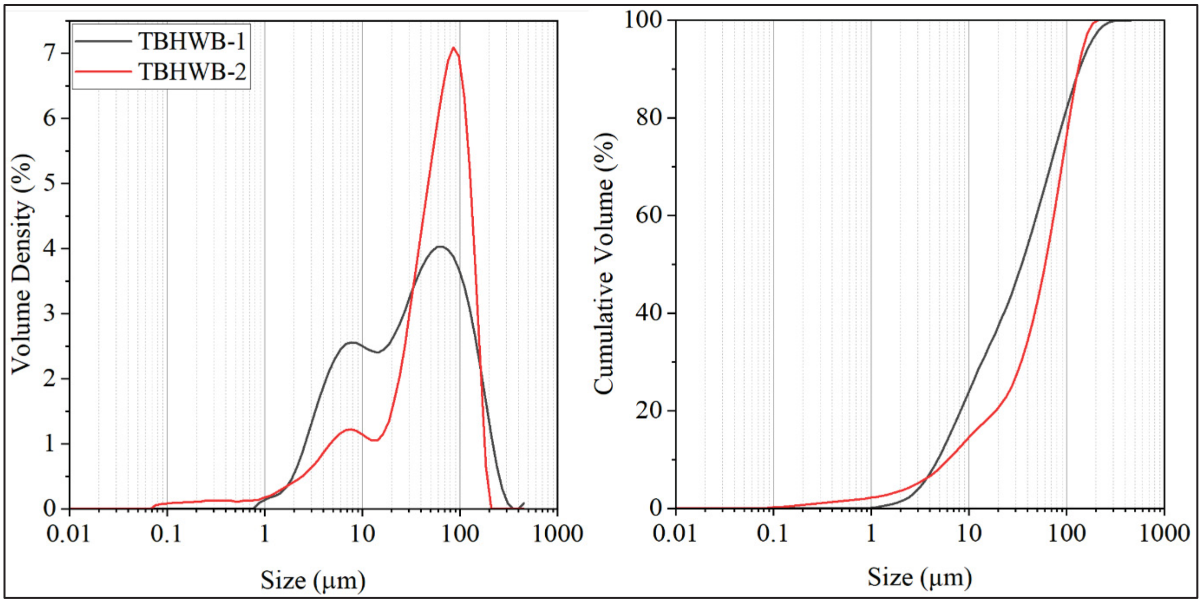


Figure 4.15 Particle size distribution of TBHWB samples

For the comparison of lignin samples from three different sources (HTSWA, KSWA-1, and TBHWA-1), as shown in Figure 4.16, the particle size distribution reveals distinct patterns unique to each lignin source. Each sample exhibits a specific PSD pattern with varying size distributions, reflecting the influence of source and processing on particle characteristics. These differences highlight the diverse granulometric properties of lignin, which may influence its behavior and applicability in various industrial contexts, specifically asphalt industry.

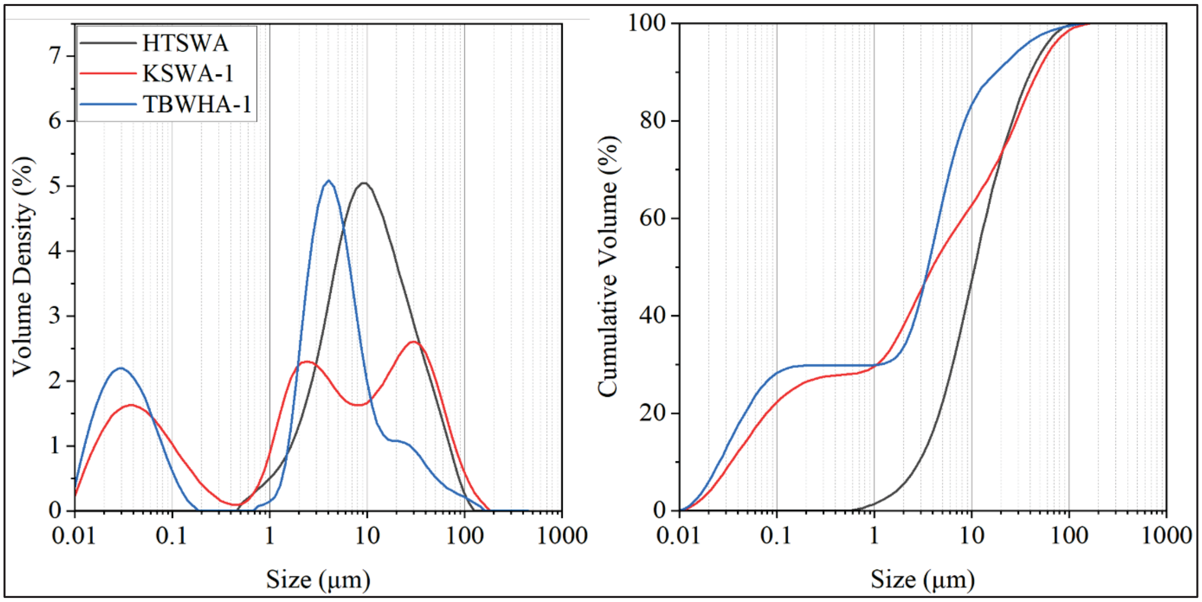


Figure 4.16 Particle size distribution of HTSWA, KSWA-1, and TBHWA-1 samples

To determine whether the type of dispersion medium influences the particle size distribution results, HTSWA and TBSWA samples were tested in both water and isopropanol. As shown in Figure 4.17 and Figure 4.18, the results indicate no significant differences between the two media, suggesting that the choice of liquid does not affect the PSD measurements for the acid-form lignin samples. This consistency demonstrates that both water and isopropanol are suitable for reliable PSD analysis.

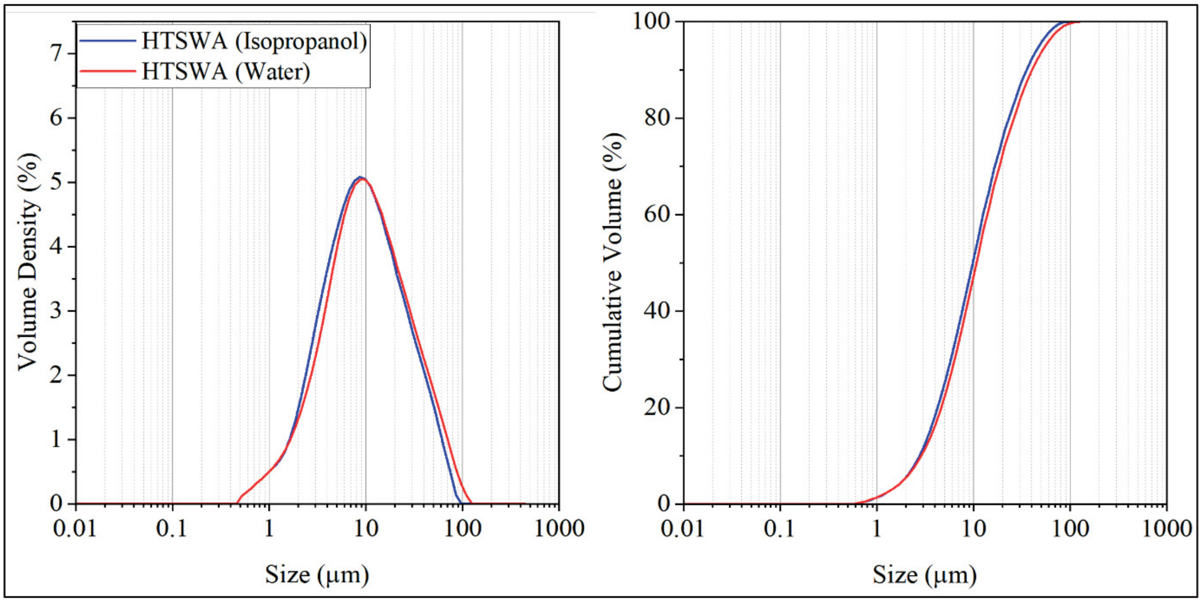


Figure 4.17 Comparison of particle size distribution of HTSWA samples using water and isopropanol as dispersion media

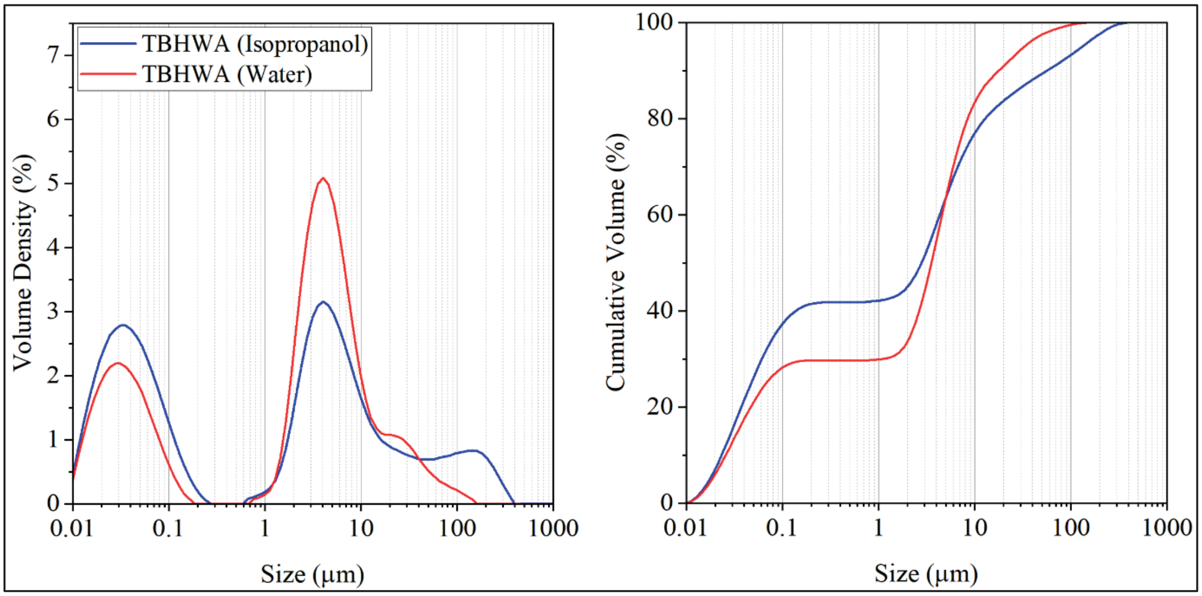


Figure 4.18 Comparison of particle size distribution of TBHWA samples using water and isopropanol as dispersion media

4.5 Conclusion

The particle size distribution (PSD) analysis and dispersion behavior of lignin samples revealed significant insights into the influence of lignin type, chemical form, processing methods, and dispersion media on their characteristics. These findings have broader implications for the potential industrial applications of lignin, including its use in asphalt modification.

- **Visual Observations and Dispersion Behavior:** The study demonstrated that acid-form and base-form lignin samples exhibit distinct dispersion behaviors in water. Acid-form lignin samples were insoluble in water, making them suitable for PSD analysis. In contrast, base-form lignin samples dissolved in water, resulting in a homogenous solution and making particle size measurements technically infeasible. Isopropanol was identified as an effective alternative dispersion medium for base-form lignins, allowing accurate particle size analysis. These observations emphasize the critical role of pH and dispersion medium selection in ensuring reliable granulometric measurements.

- **Impact of Processing Steps:** Processing methods, such as grinding and modification, were shown to influence particle size characteristics significantly. For most lignin samples, additional grinding reduced particle sizes, as seen in HTSWB and KSWB samples. However, in some cases, such as TBHWB, the second grinding step caused particle agglomeration, leading to broader PSDs. Modification processes consistently resulted in slightly coarser particles with broader distributions, highlighting the impact of chemical and physical treatments on PSD.

- **Lignin Type and Source:** Comparisons among lignin samples from different sources (HTSWA, KSWA, and TBHWA) revealed distinct PSD patterns, reflecting the inherent variability in particle size characteristics due to source-specific properties. Additionally, base-form lignins generally exhibited coarser particles than acid-form lignins, underscoring the influence of chemical form on PSD.

- **Dispersion Media:** The choice of dispersion medium (water vs. isopropanol) had negligible effects on PSD measurements for acid-form lignins, demonstrating the reliability of laser granulometry for these samples regardless of the liquid medium.

In conclusion, this phase of the project highlights the complex interplay of chemical properties, processing methods, and lignin sources in determining particle size characteristics. These insights are crucial for lignin in asphalt modification, where its role as a filler or soluble component may significantly impact material performance and stability.

CHAPTER 5

LABORATORY STUDY ON INFLUENCE OF BLENDING CONDITIONS ON CHEMO-THERMAL CHARACTERISTICS OF LIGNIN-MODIFIED BITUMEN

Ali Rezazad Gohari[a], Sébastien Lamothe[a], Jean-Pascal Bilodeau[b], Ahmad Mansourian[c] and Alan Carter[a]

[a] Département de Génie de La Construction, École de Technologie Supérieure (ÉTS), 1100 Notre-Dame Ouest, Montréal, QC, Canada, H3C 1K3.
[b] Département de Génie Civil et de Génie Des Eaux, Université Laval, 1065 avenue de la Médecine, Québec, QC, Canada, G1V 0A6.
[c] Bitumen and Asphalt Department, Road, Housing and Urban Development Research Center, Marvi St., Farhangian St., Sheikh Fazlollah Highway, Tehran, Iran, P9Q8+99J.

Paper published in *Journal of Applied Sciences*, June 2023

5.1 Abstract

Environmental approaches in the asphalt industry have focused on utilizing waste materials as modifiers. Lignin is a high-potential bitumen modifier due to its characteristics; however, the blending process with bitumen is critical. This study investigates the chemo-thermal characteristics of lignin-modified bitumen under two different blending protocols, including a mechanical and high-shear mixer to evaluate its performance as a modifier. According to the protocols, 5, 10, and 20 % of Kraft lignin was added to a PG 58S-28 bitumen. The samples were subjected to analysis using Brookfield Rotational Viscosity (BRV), Dynamic Shear Rheometer (DSR), Fourier-Transform Infrared Spectroscopy (FTIR), Environmental Scanning Electron Microscopy (ESEM), Thermogravimetric Analysis (TGA), and Differential Scanning Calorimetry (DSC) tests. The BRV and DSR test results indicate a remarkable alteration in the rheological properties of lignin-modified bitumen under blending conditions. The FTIR analysis indicated that Kraft lignin did not produce new functional groups. The fibril structures of the bitumens are affected by Kraft lignin content and blending conditions due to ESEM. The Kraft lignin and blending conditions influence the thermal behavior of bitumen. The findings highlight Kraft lignin's potential as a bitumen modifier, and the fact that its characteristics are influenced by the blending protocol and Kraft lignin content.

Keywords: kraft lignin; lignin-modified bitumen; mechanical mixer; high-shear mixer; chemo-thermal characteristics; sustainable asphalt materials.

5.2 Introduction

The use of sustainable and environmentally friendly approaches in the asphalt industry has been a major focus of recent research studies (Al-Hasan, Balamuralikrishnan, & Altarawneh, 2020). Among these approaches, the use of waste materials from other industries as modifiers or extenders in flexible pavement has gained increasing attention. One such material is lignin, which is the second most abundant biopolymer in nature (Tuck, Pérez, Horváth, Sheldon, & Poliakoff, 2012). Its unique chemical and physical characteristics make it a high-potential bitumen modifier (Gaudenzi et al., 2023). However, the blending parameters are critical factors that can significantly influence the characteristics of the resulting lignin-modified bitumen (Jamal & Giustozzi, 2022).

In this study, the chemo-thermal characteristics of lignin-modified bitumen samples produced under different blending conditions are investigated. The influence of two shear rates, obtained from a mechanical mixer (1000 rpm) and a high-shear mixer (5000 rpm), on the rheological properties, chemical reaction, and thermal behavior of the lignin-modified bitumen are evaluated. The results of this study provide insights into the influences of adding Kraft lignin and blending conditions on the characteristics of lignin-modified bitumen, which can be valuable for the development of sustainable and high-performance asphalt materials.

5.3 Background

Roads and highway networks have made the world more connected than ever before. In recent decades, increasing traffic volume has led to an undeniable demand for expanding and rehabilitating existing roads and streets. However, the road construction industry's environmental impacts cannot be ignored. Asphalt mix production has been on the rise in the United States (Williams, Willis, & Shacat, 2020), and its production and application are associated with natural resource use, energy consumption, and air pollution. Reducing global greenhouse gas (GHG) emissions is crucial for preventing climate change. "To stabilize atmospheric GHG concentrations at 400 ppmv CO_2e (the carbon dioxide equivalent), industrialized countries must reduce emissions by 25–30 % between 1990 and 2020 and by 85–90 % between 1990 and 2050" (Bramley & Chandler, 2005). Consequently, researchers have been investigating new additives and technologies that are more friendly from an environmental perspective. Among these approaches, the application of waste materials as a modifier or extender of bitumen in asphalt mix has gained popularity.

Waste materials such as lignin, crumb rubber, used oil, crushed concrete, waste plastic bottles, recycled glass, and steel slag have all been investigated (Fernandes, Costa, Silva, & Oliveira, 2017). Using waste materials, coming from municipal, urban, agricultural, or forestry sources, as a bitumen modifier is a promising approach that could significantly reduce the environmental impact of road construction. Furthermore, bio-additives have shown potential for reducing the environmental impact of asphalt production with enhanced asphalt performance. These include bio-oils derived from biomass; biopolymers, such as natural fibers and starch; and natural rubber obtained from the Hevea tree; as well as waxes and nanomaterials, such as biochar and nanoclays (Abd El-latief, 2018). However, due to the complex structure of bitumen and the reactions between modifiers or extenders, further research is needed for a better understanding of the characteristics of modified bitumen (Mansourian, Goahri, & Khosrowshahi, 2019; Porto et al., 2019).

In addition, lignin is known as the second most abundant biopolymer and naturally exists in lignocellulosic plants (Rowell, 2005). Technical lignin refers to a form of lignin obtained from the processing of biomass. The molecular weight and structure of technical lignins can vary significantly, which influences the possible applications of lignin (Bruijnincx, Weckhuysen, Gruter, & Engelen-Smeets, 2016). There are different types of technical lignins, including lignosulfonates, Kraft lignin, soda lignin, hydrolysis lignin, and Organosolv lignin (Dessbesell, Paleologou, Leitch, Pulkki, & Xu, 2020).

5.3.1 Lignin-modified Bitumen

The characteristics of lignin make it a highly promising material with potential applications in various industries. Its renewability, affordability, non-toxic nature, wide availability, and similarity in chemical structure to bitumen are key properties that make lignin a suitable modifier or alternative extender for use in the asphalt industry (Feldman, Lacasse, & Beznaczuk, 1986; J. Wu et al., 2021). In recent years, there has been a growing interest in lignin-modified bitumen.

One area of investigation has been the rheological properties of lignin-modified bitumen. Numerous studies have been conducted to evaluate the effects of several types and concentrations of lignin additives on the viscosity, stiffness, and high- and low-temperature performance of bitumen. It has been observed that the addition of lignin can improve certain properties of bitumen, such as the high-temperature performance and resistance to fatigue. However, the use of lignin can also have drawbacks, such as increased brittleness and reduced low-temperature performance (Cai et al., 2022; Gao et al., 2020; Hao Wang & Derewecki, 2013; G. Xu et al., 2017).

Al-falahat et al. conducted research to evaluate the impact of Kraft lignin as an additive at various concentrations ranging up to 30 % on the rheological properties of the bitumen (Al-falahat et al., 2024). Their test results for Brookfield Rotational Viscosity (BRV), Dynamic Shear Rheometer (DSR), Ring-and-Ball, and Multiple Stress Creep Recovery (MSCR) showed that the addition of Kraft lignin increased the viscosity, stiffness, softening point, and high-temperature performance of the bitumen, respectively. However, this also led to a decrease in low-temperature performance, as shown by their Bending Beam Rheometer (BBR) test results (Al-falahat et al., 2024).

Additionally, Cai et al. investigated the effect of lignin and formic acid lignin additives at concentrations of 5 and 10 % (Cai, Peng, & Cheng, 2023). Their study revealed that the inclusion of these additives could significantly enhance the properties of the asphalt at high temperatures, while also improving its resistance to fatigue and cracking at low temperatures (Cai et al., 2023).

Chemical reactions between lignin with bitumen and the microstructure of lignin-modified bitumen are also the subjects of some studies. Zhang et al. investigated the use of lignin as an antioxidant in bitumen and evaluated its chemical and rheological properties (Y. Zhang et al., 2019). The results of the Fourier-Transform Infrared Spectroscopy (FTIR) test on bitumen samples with 10 % Organosolv lignin showed that the various functional groups of lignin did not produce new chemical functional group peaks. Moreover, the microstructures of the bitumen with and without lignin were found to be almost identical, according to the Environmental Scanning Electron Microscope (ESEM) test (Y. Zhang et al., 2019).

In another study conducted by Zhang et al., a bio-oil was used as an additive in lignin-modified bitumen (Y. Zhang et al., 2022). FTIR spectra analysis indicated that there were no newly generated chemical functional groups in the blend of lignin, virgin bitumen, and oil. It was concluded that the blending process did not create a new chemical composition. As a result, there was either no chemical reaction or the reaction was negligible (Y. Zhang et al., 2022).

Scanning Electron Microscope (SEM) and Environmental Scanning Electron Microscope (ESEM) are important techniques for investigating lignin-modified bitumen, as they provide high-resolution images of the surface (Mazumder, Ahmed, Ali, & Lee, 2018). Many research studies have been conducted in this area (Y. Li, Lv, Cheng, Chen, & Zhang, 2023; Pasandín, Nardi, Pérez-Barge, & Toraldo, 2022; Trejo-Cáceres, Sánchez, & Martín-Alfonso, 2023). For instance, Kalampokis et al. used SEM to investigate the shape and particle size distribution of lignin powder (Kalampokis et al., 2022).

Finally, one of the noteworthy research areas of lignin-modified bitumen is the investigation of thermal properties, which are essential for its performance under high- and low-temperature conditions (Firoozifar, Foroutan, & Foroutan, 2011). The thermal stability and decomposition behavior of lignin-modified bitumen can be assessed using Thermogravimetric Analysis (TGA). Numerous research studies have been conducted to investigate the thermal properties of modified bitumen (Asif, Ahmad, Asif, Zaidi, & Amin, 2023; Ishaq & Giustozzi, 2023; Xia, Xia, Xu, Zhang, & Li, 2023). For example, Nizamuddin et al. used TGA to investigate the effect of low-density polyethylene (LDPE) on the thermal stability of bitumen, and their results showed that blends with a higher percentage of recycled LDPE were more thermally stable and exhibited a low rate of evaporation compared to blends with low LDPE concentrations (Nizamuddin, Jamal, Biligiri, & Giustozzi, 2024). Jianfei et al. investigated the combustion properties of lignin residues using TGA. The results showed that washing processes changed the thermal characteristics of lignin samples (Jianfei, Zixing, Liangmeng, Qi, & Zhijia, 2020).

Another important research area in the study of lignin-modified bitumen is the use of Differential Scanning Calorimetry (DSC) testing to evaluate its thermal properties, including the glass transition temperature (T_g) and degree of crystallinity (G. Memon & Chollar, 1997; Pipintakos, Soenen, Goderis, Blom, & Lu, 2022). The glass transition temperature (T_g) and degree of crystallinity are critical factors in assessing and determining the performance characteristics of bitumen (Laukkanen, Soenen, Winter, & Seppälä, 2018). Numerous research studies have employed DSC testing to investigate these properties in modified bitumen (Apostolidis, Elwardany, Andriescu, Mensching, & Youtcheff, 2023; Lei, Yi-qiu, & Bahia, 2016; Lucena et al., 2004).

Wręczycki et al. investigated the potential of sulfur/organic copolymers as modifiers for bitumen binders (Wręczycki et al., 2022). Glass transition temperature (T_g) was one of the properties studied in their research. The incorporation of sulfur/organic copolymers was found to cause a significant decrease in T_g, by up to 4 °C, indicating that the copolymers interacted with the bitumen and altered its properties. This finding suggests that sulfur/organic copolymers have the potential to improve the low-temperature performance of bitumens (Wręczycki et al., 2022).

5.3.2 Blending Protocols for Lignin-Modified Bitumen

Blending protocols play a critical role in determining the properties of lignin-modified bitumen, as they have a significant influence on the physicochemical characteristics and performances of the final product (Jamal & Giustozzi, 2022). The blending conditions, such as blending temperature, time, and shear rate, can significantly affect the interaction and distribution of lignin in bitumen (Jamal & Giustozzi, 2020). Numerous studies have been conducted on lignin-modified bitumen prepared with various blending protocols. Understanding the blending conditions and efficiency is crucial for ensuring the optimal performance and properties of lignin-modified bitumen. Table 5.1 summarizes the variety of blending protocols used in these studies to investigate the properties of lignin-modified bitumen.

Table 5.1 Various blending protocols of lignin and bitumen in the literature

Mixer (Type)	Additive (Type)	Bitumen (Type)	Blending Temp. (°C)	Blending Time (min)	Shear Rate (rpm)	Ref.
High-shear mixer (HSM)	Lignin	Grade 60/70	155	30	5000	(Zahedi, Zarei, & Zarei, 2020; Zahedi, Zarei, Zarei, & Janmohammadi, 2020)
		Grade 70/100	163	30	3000	(Y. Zhang et al., 2022)
			160	120	3000	(Ren et al., 2021)
		Grades 50/70 and 160/220	150	60	6000	(Norgbey et al., 2020)
		PG 58–28	160	40	6000	(Gao et al., 2020)
		---	130	45	5000	(R. Zhang, Sun, et al., 2021)
		---	155	30	5000	(Zarei et al., 2019)
	Kraft lignin	Grade 50/70	160	60	5000	(K. Batista et al., 2018)
		PG 67–22	180	30 + 30	4000 + 8000	(Arafat et al., 2019)
		PG 64–22	160	60	5000	(Fakhri & Norouzi, 2022)
	Wood lignin	Grade 70	160–168	45	1200	(J. Wu et al., 2021)
		Grade 70/100	163	30	3000	(Y. Zhang et al., 2019)
	Organosolv lignin	Grade 70/100	163	30	3000	(Y. Zhang, Liu, et al., 2020)
	Soda lignin	Grade 60/70	155	10 + 50	4000 + 8000	(Yu et al., 2021)
	Kraft lignin and Corn stalk lignin	Grade 60/70	160	60	4000	(C. Xu et al., 2021)
	Alkali lignin and quercetin	PG 64–22	170	45	4500	(D. Hu et al., 2022)
Mechanical mixer (MM)	Kraft lignin	Grade 50/70	160	30	2000	(Duarte Mendonça et al., 2022)
		PG 58S–28 and PG 52S–34	170	15	1000	(Al-falahat et al., 2024)
	Wood lignin	PG 64–22 and PG 76–22	163	30	1500	(G. Xu et al., 2017)
	Lignin	---	140	60	1000	(He et al., 2022)

In light of the growing interest in the development of sustainable and environmentally friendly approaches in the asphalt industry, the utilization of waste materials as modifiers or extenders in bitumen has emerged as a promising strategy for reducing the environmental impact. Among these waste materials, lignin, a widely available and renewable biopolymer, has garnered considerable interest due to its chemical and physical properties that make it a promising material for bitumen modification. Previous studies have investigated the rheological properties, chemical reactions, microstructure, and thermal behavior of lignin-modified bitumen, revealing both potential benefits and challenges associated with its use. However, further research is needed to elucidate the blending protocols and their influence on the performance of lignin-modified bitumen.

5.4 Laboratory Study

In this laboratory study, different amounts of a single type of lignin were added to a single type of bitumen with two different blending protocols. The lignin-modified bitumens produced were then tested to evaluate their viscosity and their viscoelastic properties before testing their chemical and thermal properties. The description of the materials, the blending protocols, and the different tests used are shown hereafter.

5.4.1 Materials

5.4.1.1 Bitumen

In this research study, an unmodified bitumen PG 58S−28 for a standard traffic level (S), obtained from Bitumar, a Canadian company, was utilized. All specifications and test results provided by the manufacturer are presented in Table 5.2.

Table 5.2 Tests and specifications of PG 58S–28 based on the manufacturer's data sheet

Characteristic (Unit)	**Amount**	**Specification Limits**	**Standard or Test Method**
Flashpoint (°C)	273	>230	ASTM D 92
Density at 25 °C (g/cm^3)	1.021	1.000–1.050	AASHTO T 228
Density at 15 °C (g/cm^3)	1.027	1.007–1.037	AASHTO T 228
Brookfield viscosity at 135 °C (mPa·s)	309	150–500	AASHTO T 316
Brookfield viscosity at 165 °C (mPa·s)	92	30–180	AASHTO T 316
Storage stability (°C)	0.3	≤2.0	LC 25-003
Ash content (%)	0.28	≤0.50	ASTM D 8078
|G*|/Sinδ at 58 °C (kPa)	1.54	≥1.00	AASHTO T 315

5.4.1.2 Kraft Lignin

The Kraft lignin utilized in this study is a sticky brown fine powder, derived from softwood and provided by FPInnovations (Figure 5.1a). Kraft lignin is a valuable and sustainable raw material produced as a byproduct of the paper industry. The main properties of this powder are presented in Table 5.3. The elemental analysis provided by the supplier indicated that the Kraft lignin was composed primarily of four (4) main elemental components, including carbon, hydrogen, oxygen, and sulfur, with the remaining 3 % composed of other elements (Figure 5.1b).

Table 5.3 Properties of the used Kraft lignin provided by the supplier

Property (Unit)	**Value**
Density (g/cm^3)	1.2–1.3
Potential Hydrogen (pH)	3–4
Molecular Weight (g/mol)	5185
Moisture Content (%)	1.3
Ash Content at 575 °C (%)	0.42
Purity (%)	95

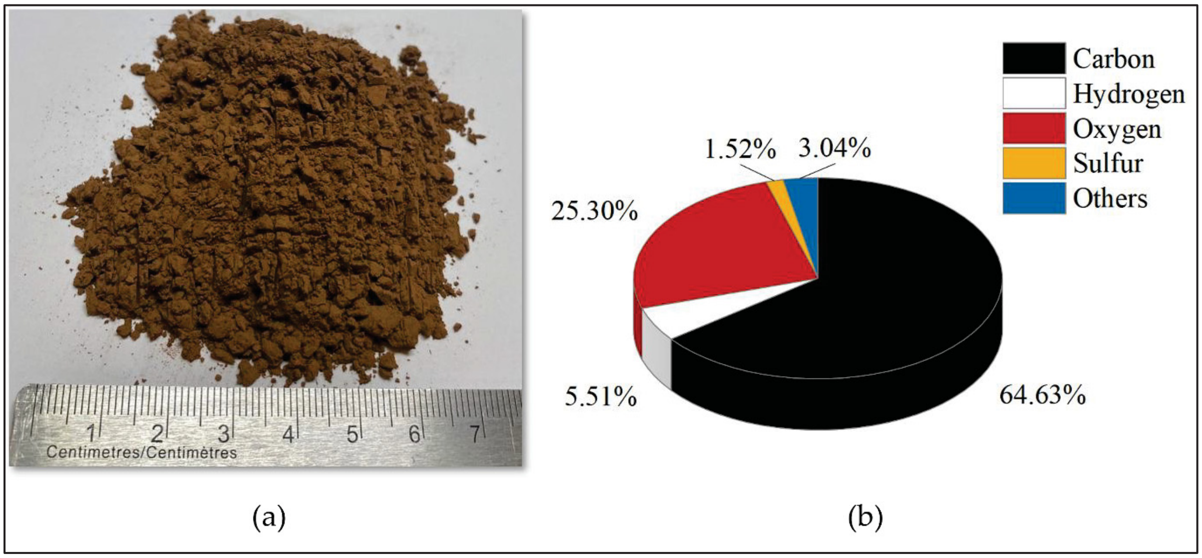
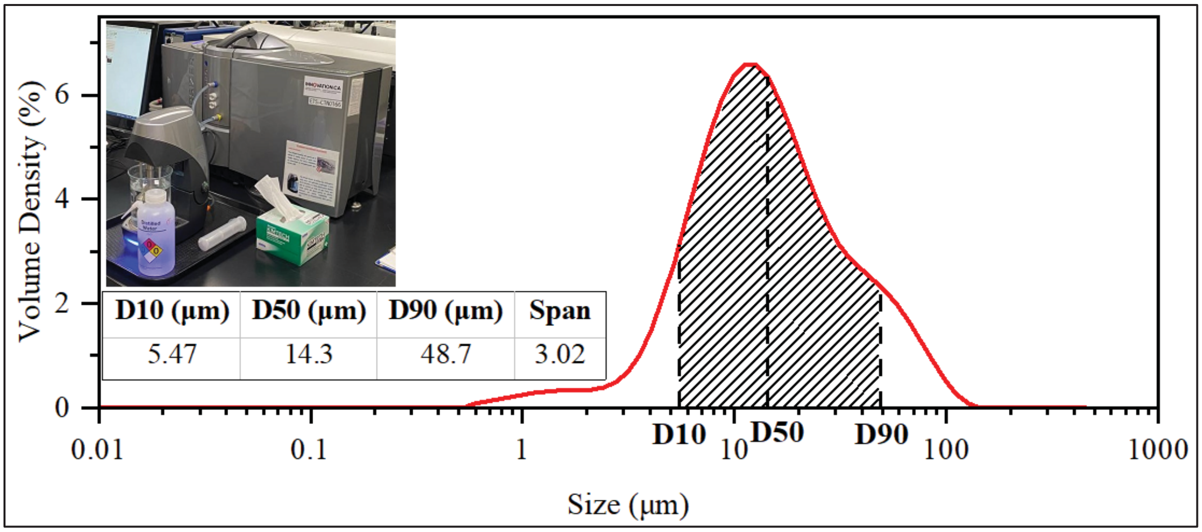


Figure 5.1 (a) Studied Kraft lignin powder and (b) Elemental analysis of Kraft lignin

Particle size distribution is a critical property that can influence the performance of materials in various applications. To determine the particle size distribution of Kraft lignin, the laser diffraction technique was employed using a Mastersizer 3000 instrument equipped with a Hydro EV dispersion unit. The measurements were conducted over a range of 0.01–500 µm to ensure a comprehensive analysis of the particle size distribution. The resulting data showed that the particle size of the Kraft lignin powder fell within the range of 1 to 100 µm, with 80 % of the particles between 5.47 µm (D10) and 48.7 µm (D90), as shown in Figure 5.2.



D10 (µm)	D50 (µm)	D90 (µm)	Span
5.47	14.3	48.7	3.02

Figure 5.2 Particle size distribution of Kraft lignin determined by laser diffraction technique

5.4.2 Sample Preparation and Blending Protocols

The main aim of this research study is to investigate the influence of Kraft lignin as a bitumen modifier on the chemo-thermal characteristics of the lignin-modified bitumen, as well as the influence of different blending conditions. To achieve this, Kraft lignin was added to the bitumen at three (3) different percentages of 5, 10, and 20 % (Table 5.4) by weight of the lignin-modified bitumen (lignin + bitumen). According to the recently published article by our colleague, the maximum mass percentage of this specific lignin (Kraft lignin: acidic and derived from softwoods) with an unmodified bitumen (PG 58S−28 or PG 52S−34) and mixed with a mechanical mixer is 30 %; otherwise, the storage stability and homogeneity of the bitumen–lignin blend are affected negatively (Al-falahat et al., 2024). In addition, two (2) types of mixers were utilized in this study, an IKA RW16 Basic Overhead Stirrer, with a maximum rate of 1200 rpm, referred to as the mechanical mixer (MM), and a Silverson L4RT high-shear mixer (HSM), with a maximum rate of 8000 rpm, as shown in Figure 5.3. This study focuses on the effect of the shear rate as the research parameter, with two (2) different rates investigated: 1000 and 5000 rpm. The blending time was fixed at 60 min, and the blending temperature was maintained at 150 ± 5 °C throughout the blending process by an oil bath. Prior to the blending process, the bitumen samples were placed in an oven at 150 °C to achieve a uniform blending temperature. Subsequently, the beaker containing the bitumen was suspended in an oil bath for 20 min to stabilize the bitumen temperature before the addition of Kraft lignin. Due to the sticky nature of Kraft lignin, the addition process of the additive was carried out gradually within 15 min, followed by 45 min of blending time, for a total of 60 min. In order to enhance the accuracy and comparability of test results, two (2) virgin bitumen specimens were processed using the same blending protocols without the addition of Kraft lignin, referred to as VB-MM for the mechanical mixer and VB-HSM for the high-shear mixer. The samples in this study were named according to Table 5.4.

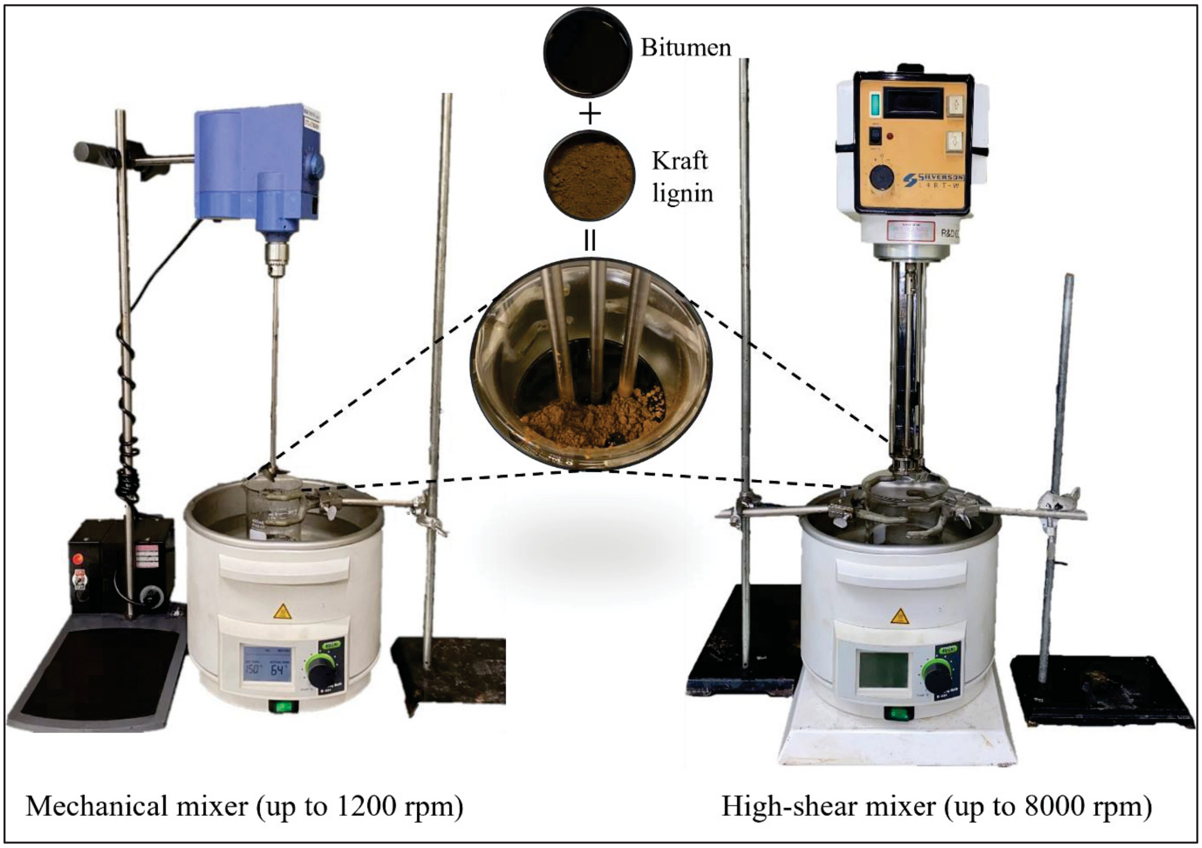


Figure 5.3 Blending Kraft lignin and bitumen using Mechanical Mixer (MM) and High-Shear Mixer (HSM) in the oil bath

Table 5.4 Details of specimens tested in the study

Sample Details	**Kraft Lignin (wt %)** [1]	**Blending Protocol**	**Code**
Virgin Bitumen (VB)	0	---	VB
		MM	VB-MM
		HSM	VB-HSM
Bitumen with added Kraft lignin (L)	5	MM	5L-MM
		HSM	5L-HSM
	10	MM	10L-MM
		HSM	10L-HSM
	20	MM	20L-MM
		HSM	20L-HSM

[1] The lignin content is a percentage of the total weight of the lignin-modified bitumen (lignin + bitumen).

5.4.3 Testing

5.4.3.1 Brookfield Rotational Viscosity (BRV) Test

In this study, the influence of Kraft lignin, as an additive, on the viscosity of modified bitumen was evaluated, as the fine powder nature of lignin can significantly modify this property of bitumen.

The viscosity of bitumen samples was determined using a Brookfield Rotational Viscometer (BRV) device, which characterizes the bitumen for workability during pumping, mixing with aggregate, and compaction of hot mix asphalt. To perform the BRV test, a cylindrical spindle was rotated inside a container filled with bitumen at a specified speed. To determine the viscosity of bitumen, the torque needed to maintain a constant rotational speed of the spindle was measured. A Brookfield DV2T viscometer produced by Ametek-Brookfield was used in this study. The BRV test was conducted following the test procedures described in the LC 25-007 Quebec test method, at 135 and 165 °C for all samples. The bitumen samples were poured into a cylindrical container and placed in the device at a temperature of 135 followed by 165 °C. Nine (9) readings were recorded at 1 min intervals.

5.4.3.2 Dynamic Shear Rheometer (DSR) Test

In this laboratory study, the Dynamic Shear Rheometer (DSR) test was conducted to evaluate the linear viscoelastic (LVE) properties of unaged bitumen samples. The DSR test was carried out according to the AASHTO T315 standard, using a Kinexsus DSR produced by Malvern. A sinusoidal shear load with a loading frequency of 10 rad/s was applied on a 25 mm diameter plate with a sample thickness of 1 mm. The test was conducted at 58, 64, and 70 °C. Rheological parameters, such as the norm of the complex shear modulus ($|G^*|$) and phase angle (δ), were determined. Additionally, $|G^*|/\sin\delta$ values were calculated to evaluate, to some extent, the rutting resistance of the bitumen samples.

5.4.3.3 Fourier-Transform Infrared Spectroscopy (FTIR) Test

The chemical composition of bitumen is complex and multifaceted due to the diverse origins of crude oil resources. The addition of modifiers to enhance the mechanical properties of bitumen results in further complexity in its chemical characteristics.

Fourier-transform infrared spectroscopy (FTIR) is a commonly used and appropriate analytical technique for detecting chemical compounds and obtaining information on the chemical composition of materials at the molecular level. It has the potential to yield both qualitative and quantitative outcomes, which could be valuable for research studies. This study investigates the chemical interactions between bitumen and Kraft lignin. When two materials are in contact, their molecular vibrations can change due to chemical interactions. These changes can be detected by comparing the FTIR spectra of the individual materials with the FTIR spectra of the mixture. In this study, attenuated total reflectance ATR-FTIR was used to gather spectral information from Kraft lignin and bitumen samples. The Spectrum Two™ FTIR Perkin Elmer, which incorporates a Diamond crystal, was employed to obtain data within the wavenumber range of 4000 to 400 cm^{-1} at a 4 cm^{-1} resolution. Twenty (20) scans were recorded for each spectrum. Prior to each test, the ATR crystal was cleansed using limonene and isopropanol, and a background spectrum was captured.

5.4.3.4 Environmental Scanning Electron Microscope (ESEM) Test

The intricate behavior of bitumen is influenced by both its chemical composition and microstructure. This fact motivates researchers to investigate bitumen structures at the micro and nano scales, using various technologies to establish the relationship between microstructure and physical properties.

Environmental Scanning Electron Microscopy (ESEM) is a type of electron microscopy that enables the imaging of oily materials, such as bitumen, in their natural state. This technique eliminates the need for bitumen conductive coating processes and ultra-high vacuum typically required for conventional Scanning Electron Microscopy (SEM) (Mazumder et al., 2018). ESEM can be used to investigate the morphology and dispersion of modifiers within the bitumen matrix, aiding in a better understanding of its behavior. In this study, the protocol developed by Mikhailenko et al. was followed (P Mikhailenko, Kadhim, Baaj, & Tighe, 2017). The bitumen samples were softened at 150 °C for 30 min. Approximately 0.5 to 1 g of bitumen was poured into 8 mm diameter and 2 mm height stainless steel molds using a spatula. The sample then was flattened by placing the mold on a hotplate to ensure a flat surface. Observations were conducted at room temperature using a FEI Quanta 250 FEG ESEM. The test parameters were set up with an acceleration voltage of 20 keV, a chamber pressure of 0.8 mbar in low vacuum mode, and a magnification of ×1000 in secondary electron (SE) mode.

5.4.3.5 Thermogravimetric Analysis (TGA) Test

Thermogravimetric Analysis (TGA) is one of the methods to study the thermal properties of materials. The sample weight change is measured at a given temperature and time while the temperature is rising under a constant heating rate. The sample could lose weight due to the decomposition and debonding of the structural components or gain weight due to an instant gas reaction. Thermograms of TG and derivatives thermogravimetric (DTG) provide valuable information. DTG curves are the first differential of TG curves, which is an indicator of the degradation rate at a given temperature. Different interpretations and multifunctional analyses can be made from this information to investigate thermal characteristics of the material. The thermal and oxidative stability, durability of material against temperature, determining the multi-component material according to degradation stages, kinetic reaction, amount of volatile component, and moisture, are the most crucial parameters that could be identified. In this laboratory study, the TGA test was conducted with the STA8000 PerkinElmer's device under air atmosphere for Kraft lignin powder and bitumen samples. The testing temperature range was considered from room temperature to 1000 °C, with a heating rate of 10 °C/min and a gas flow of 50 mL/min.

5.4.3.6 Differential Scanning Calorimetry (DSC) Test

Another technique commonly used to investigate the thermal behavior of materials is Differential Scanning Calorimetry (DSC). This technique provides valuable information about the physical, chemical, and thermal properties of materials by measuring the heat absorbed or released during a controlled heating or cooling process. DSC works on the principle of differential heat flow measurement, where a sample and a reference material are subjected to the same controlled temperature program. Any difference in heat flow between the sample and reference is measured and plotted as a function of temperature. The DSC test was performed on 5–10 mg of material in an aluminum hermetic pan. A nitrogen (N_2) atmosphere with a flow rate of 50 mL/min was maintained throughout the test using the DSC2500 instrument from TA

Instruments. The samples were prepared by cutting them into small pieces and placed in a pan. The pan and the pierced lid were crimped using a press.

The samples were subjected to four (4) temperature cycles, ranging from −80 to 160 °C, to accurately characterize their thermal properties (Figure 5.4). The 1st cycle aimed to facilitate proper contact between the bitumen sample and the pan by softening the bitumen. To achieve this objective, the samples were subjected to a temperature increase from room temperature to 130 °C, with a heating rate of 20 °C/min. The 2nd cycle involved a temperature decrease to −80 °C, with a rate of 10 °C/min, followed by an increase to 160 °C. This cycle aimed to eliminate any thermal history in the samples. In the 3rd cycle, the temperature again dropped to −80 °C to eliminate the cold crystallization effect. The last and 4th cycle had a slightly different setup from the others. As reported in the Apostolidis et al. research, their study showed that Temperature Modulation-DSC (TM-DSC) is a more accurate technique than Temperature Linear-DSC (TL-DSC) for analyzing bitumen (Apostolidis, Elwardany, Porot, Vansteenkiste, & Chailleux, 2021). They also found that TM-DSC can detect the glass transition (T_g) region in bitumen with high precision. As a result, for the 4th cycle, the TM-DSC protocol was set up with a heating rate of 5 °C/min, with ±0.5 °C modulation every 80 s.

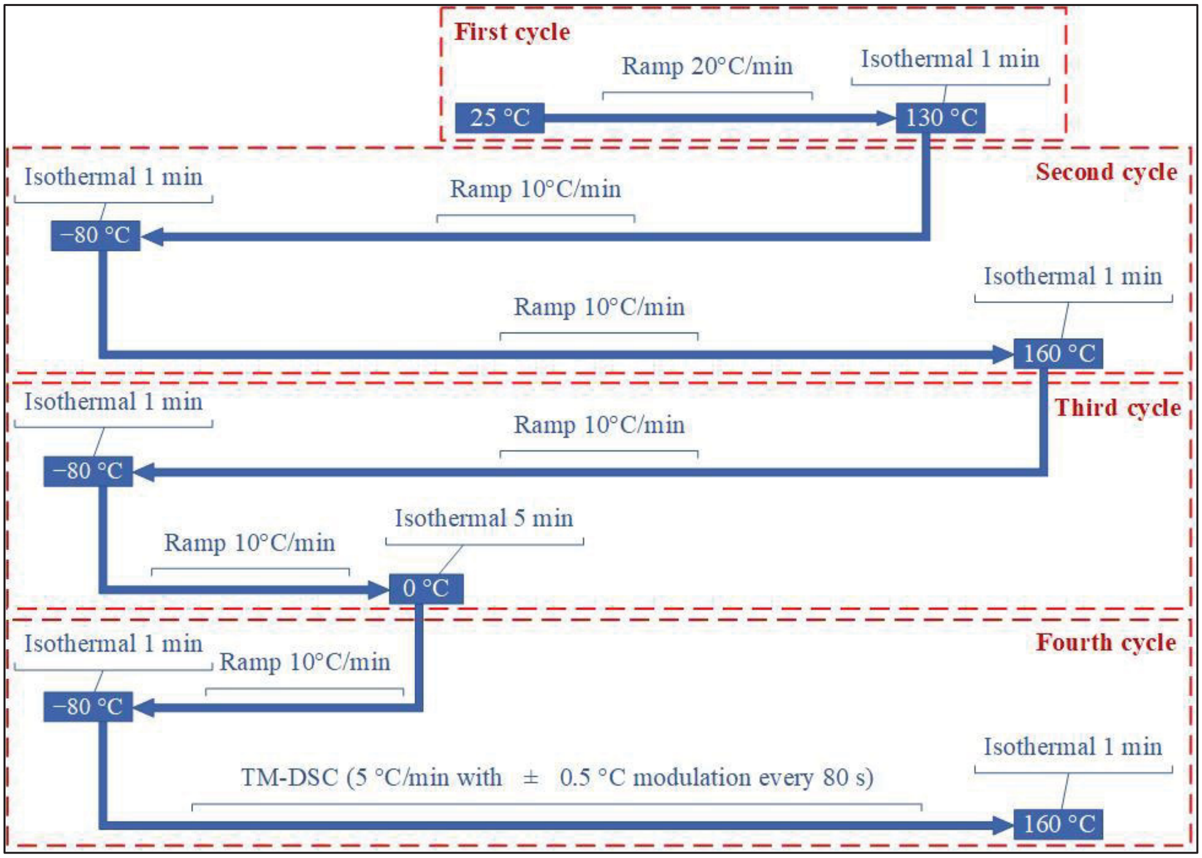


Figure 5.4 DSC methodology for samples

5.5 Results and Discussion

5.5.1 BRV Results

The BRV test results for all bitumen samples at 135 and 165 °C are shown in Figure 5.5. The results show the influences of Kraft lignin with different percentages and blending conditions on the rotational viscosity of the bitumen samples. More precisely, the measured viscosities allow quantifying the influence of Kraft lignin, as an additive, on the stiffness of bitumen, specifically at a high percentage of additive.

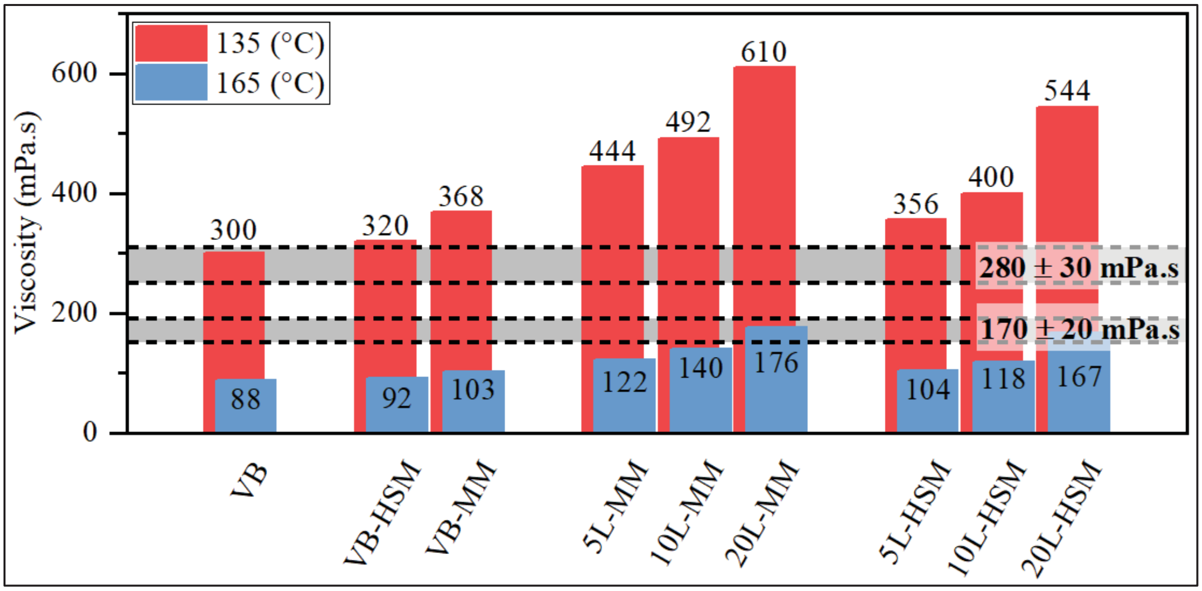


Figure 5.5 The viscosity of bitumen samples at 135 and 165 °C

Generally, adding Kraft lignin increases the viscosity of the virgin bitumen at 135 and 165 °C and enhances the high-temperature stability. As seen in Figure 5.5, the viscosity of virgin bitumen at 135 °C is 300 mPa·s, which is similar to what the manufacturer measured (value of 309 mPa·s: Table 5.2). The addition of 5, 10, and 20 % of Kraft lignin using a high-shear mixer (HSM) increase the viscosity to 356, 400, and 544 mPa·s, respectively. Likewise, samples prepared using a mechanical mixer (MM) exhibit a similar trend (444, 492, and 610 mPa·s for 5, 10, and 20 % of Kraft lignin, respectively).

The mechanisms behind the observed increase in viscosity may relate to the molecular weight of Kraft lignin and bitumen. According to the producer's data sheet, the molecular weight of Kraft lignin is 5185 g/mol. Bitumen has a wide range of molecular weights, depending on the crude oil source and composition, but it seems that bitumen has a lower molecular weight than Kraft lignin. This increase in molecular weight may lead to higher viscosity. In addition, the polarity of Kraft lignin may be a potential factor influencing the rheological properties of the modified bitumen. As bitumen is known to possess a relatively high polarity, the presence of Kraft lignin may further contribute to the increase in viscosity. Moreover, Kraft lignin is a powder, so it contains solid particles, which increases the viscosity.

The influence of the shear rate on viscosity is significant. Samples prepared by a high-shear mixer (HSM) show a lower viscosity compared to the mechanical mixer (MM) samples. Figure 5.5 illustrates the impact of the shear rate on virgin bitumen. Processing virgin bitumen using a high-shear mixer (HSM) results in a 7 % increase in viscosity, whereas using a mechanical mixer (MM) increases it by 23 %. The difference in viscosity could be attributed to a greater loss of volatiles from the virgin bitumen processed by the MM. When blending Kraft lignin with bitumen using a MM, which has a three-bladed head, the rotational motion of the mixer creates a centrifugal force that pushes the bitumen outward, resulting in a non-flat surface with a funnel shape. This shape increases the surface area of the bitumen in contact with air, leading to higher oxidation (Figure 5.6a). However, HSM has a different head design that creates a flat surface on the bitumen during blending (Figure 5.6b). This flat surface reduces the contact area of the bitumen with air, thus reducing the possibility of oxidation. Further, the selection of an appropriate head for a high-shear mixer may influence the properties of the final product. Among the various heads available, the widely used head for powder materials was used. An HSM could lead to reduced stiffness and oxidation during the blending process compared to a MM.

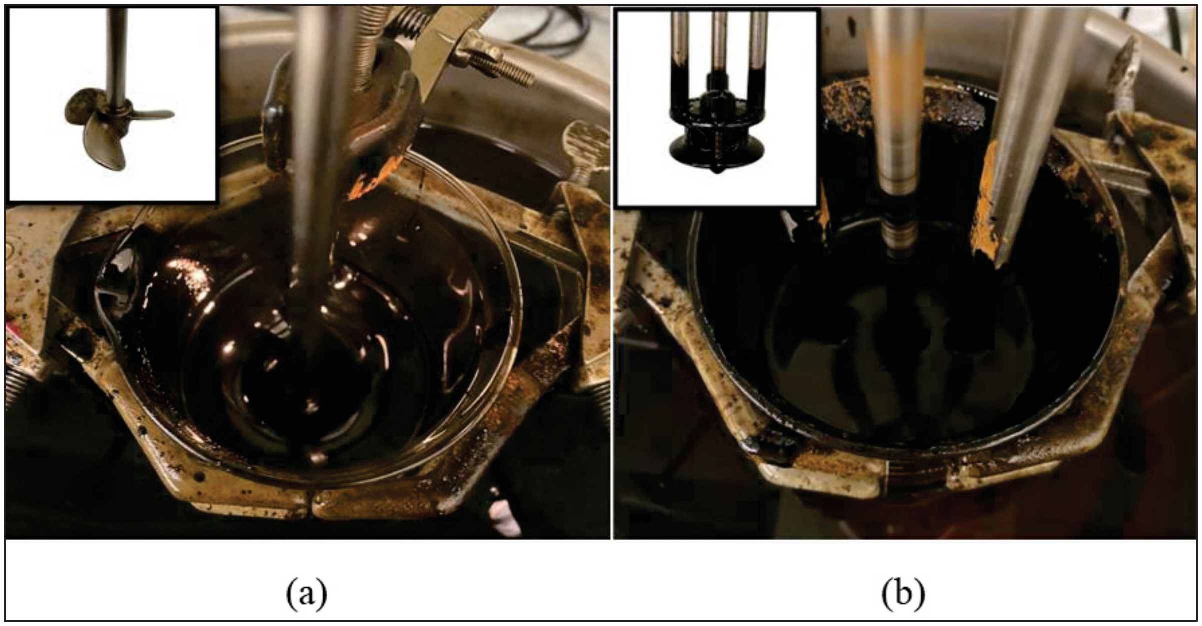


Figure 5.6 Comparison between (a) the mechanical mixer (MM) and (b) the high-shear mixer (HSM) during blending process

In general, according to the test results, all samples that were processed in either mixer have higher viscosity. According to the LC 25-007 test method, the required viscosity for mixing and compaction is 170 ± 20 mPa·s and 280 ± 30 mPa·s, respectively, for binder used for hot mix asphalt (HMA) (limits presented in Figure 5.5). To achieve these target values, it is necessary to increase the mixing and compaction temperature. Due to its higher viscosity, bitumen requires higher temperatures to become sufficiently fluid for mixing and compaction, resulting in higher energy consumption. It is noteworthy that the viscosity of both virgin and modified bitumens does not exceed the prescribed limit of 3000 mPa·s at 135 °C, as specified by AASHTO M320.

5.5.2 DSR Results

Figure 5.7 and Figure 5.8 depict the results of the dynamic shear rheometer (DSR) test conducted on unaged bitumen samples. The DSR test results indicate a remarkable modification in the rheological properties of lignin-modified bitumen under different blending conditions.

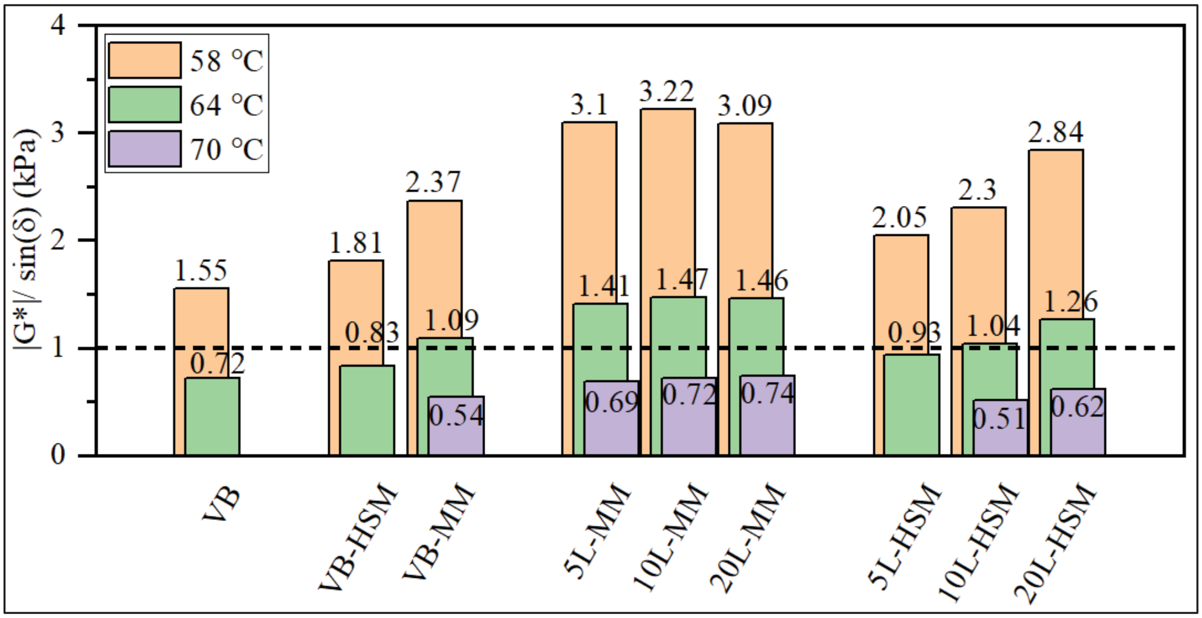


Figure 5.7 Impact of Kraft lignin on the |G*|/sinδ of bitumen under two blending conditions (dotted line: minimum value at 58 °C)

The variation of |G*|/sin(δ) with temperature for bitumen with different Kraft lignin contents (0, 5, 10, and 20 %) in different blending conditions is shown in Figure 5.7. The |G*|/sin(δ) parameter is an indicator of the rutting resistance of an asphalt binder. Furthermore, it is essential to note that the value of |G*|/sin(δ) in the DSR test should surpass 1.00 kPa for unaged asphalt binders, as specified by the Performance Grade (PG) standards for bitumen (Ministère des Transports du Québec: 4101 standard). The results indicate an increasing trend in the value of |G*|/sin(δ) for all bitumen samples, compared to the VB sample. The samples without Kraft lignin show a significant increase in stiffness (|G*|value increasing) and in elastic behavior (δ value reducing) during the blending process, which is noteworthy, with a rise, for the |G*|/sin(δ) parameter, from 1.55 kPa for VB to 1.81 and 2.37 kPa for VB-HSM and VB-MM, respectively, at 58 °C. As the addition of Kraft lignin results in an upward shift in |G*|/sin(δ), it indicates an increase, to a certain extent, in the rutting resistance. This increment is more prominent in MM samples than in HSM samples, which suggests that in the MM blending process, as previously discussed, more volatile and light components were lost and exhibited more stiffness (|G*|) and less viscous behavior (δ) in general. Therefore, it can be concluded that the addition of Kraft lignin significantly enhances the rutting resistance of bitumen, and the blending process also affects the |G*| and δ. For more information on the effect of lignin on rutting resistance, refer to Al-falahat et al. (2024). For instance, the HSM samples exhibit increases of 32, 48, and 83 % for the 5L-HSM, 10L-HSM, and 20L-HSM samples, respectively, for the |G*|/sin(δ) parameter, which is an indicator for rutting resistance.

Figure 5.8 illustrates the norm of the complex shear modulus (|G*|) and the phase angle (δ) of all samples, indicating a significant modification for the HSM and MM samples in different ways. An increase in the |G*| value indicates that the lignin-modified bitumen samples are becoming stiffer. A decrease in δ values suggests that the samples are becoming more elastic and less viscous, as they are able to respond more quickly to the applied stress.

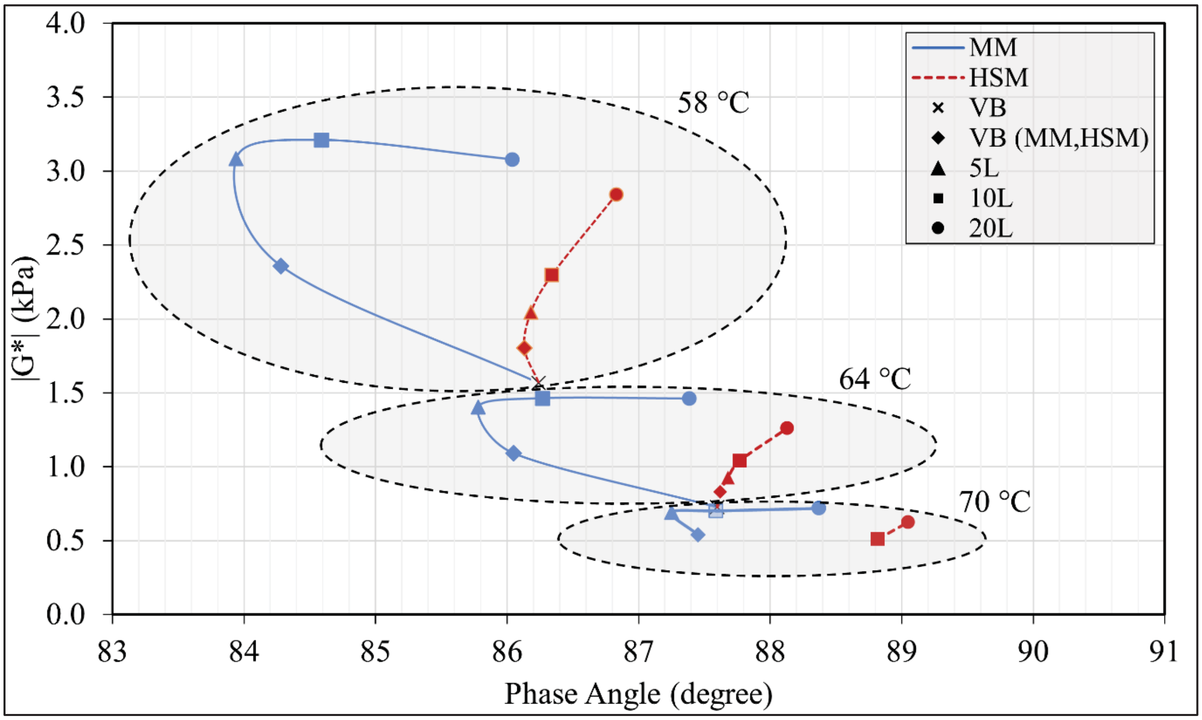


Figure 5.8 Norm of complex shear modulus |G*| and phase angle (δ) of specimens using DSR test

Regarding the impact of Kraft lignin as an additive, the results show that adding Kraft lignin in the HSM samples leads to a significant increase in stiffness (|G*|), but does not have a significant effect on the viscous behavior (a small change in the δ value) (Figure 5.8). Conversely, the MM samples exhibit less alteration in |G*| (stiffness), but remarkable changes in the δ (viscous behavior). For instance, in HSM samples at 58 °C, the δ value changes by −0.07, 0.12, and 0.68 % (less than 1 %) for 5, 10, and 20 % of Kraft lignin, respectively. All changes suggest that the addition of Kraft lignin using HSM does not have a remarkable impact on δ. However, the changes in |G*| are remarkable. The HSM blending process itself leads to an increase in |G*| by 15 % at 58 °C. Furthermore, the addition of 5, 10, and 20 % of Kraft lignin results in a significant increase in |G*| by 31, 47, and 81 %, respectively, at 58 °C. For MM samples at 58 °C, the blending process increases the |G*| by 51 %. Meanwhile, by increasing the Kraft lignin percentage, |G*| increases by 97, 105, and 97 % for the 5L-MM, 10L-MM, and 20L-MM samples, respectively.

Lastly, in terms of blending conditions, samples prepared with a MM exhibited higher |G*| and lower δ values compared to those prepared with HSM (Figure 5.8). These findings indicate that the MM samples have greater stiffness and elasticity than the HSM samples. It is important to note that the HSM samples exhibit a distinctly different behavior compared to the MM samples. These findings highlight the significant impact of blending conditions on the rheological behavior of modified bitumen with Kraft lignin. Further, it can be concluded that the MM samples undergo more extensive oxidation and aging. These observations align with the results obtained from the BRV tests.

5.5.3 FTIR Results

The FTIR spectroscopy analysis was performed to investigate the influence of Kraft lignin addition on the chemical structure of bitumen under different blending conditions. Figure 5.9 shows the FTIR spectral results of VB and HSM samples. The FTIR spectrum presented in this study was obtained as an average of three (3) replicates. To ensure consistency and comparability, all spectra were normalized to the band with the highest intensity in the bitumen spectrum using a min–max normalization approach (Mirwald, Nura, & Hofko, 2022).

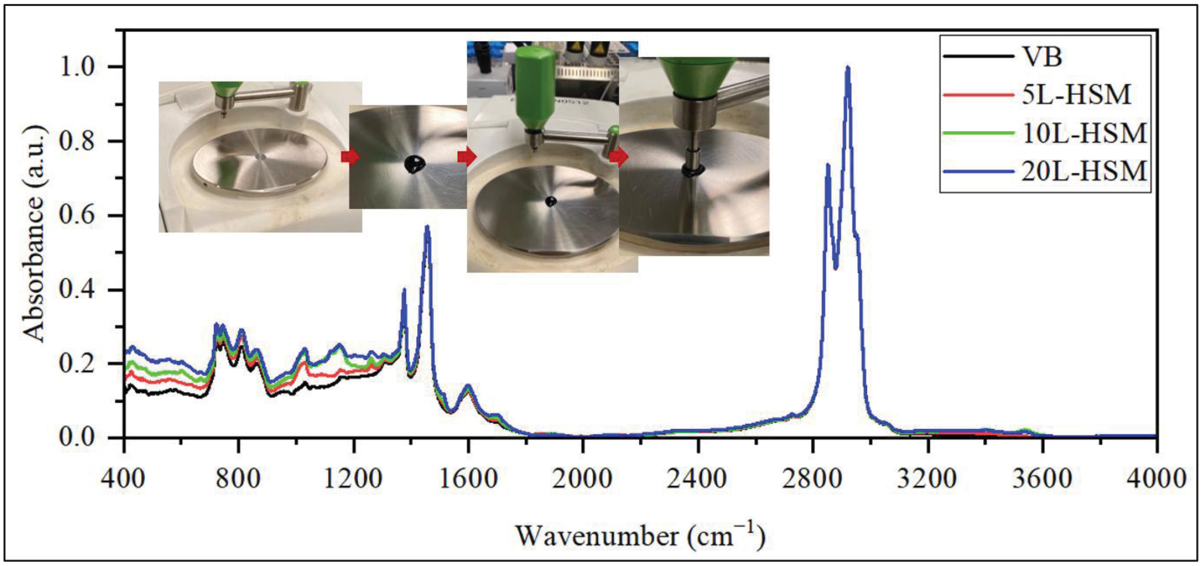


Figure 5.9 FTIR spectra of VB, 5L-HSM, 10L-HSM, and 20L-HSM binders (wavenumber of 400 to 4000 cm^{-1})

As shown in Figure 5.9, significant changes observed are between 2000 to 400 cm^{-1}, which are typically referred to as the "fingerprint region" (Peter Mikhailenko, Bertron, & Ringot, 2016). This region contains a unique pattern of absorption peaks that can identify specific functional groups present in the modified bitumen sample.

From a chemical reaction point of view, the FTIR spectra of Kraft lignin and modified bitumen with 5, 10, and 20 % of Kraft lignin for HSM samples in the fingerprint region are shown in Figure 5.10. A shift to higher wavenumbers (2000 to 400 cm^{-1}) in an FTIR spectrum can indicate a change in chemical structure and an increase in bond strength but does not necessarily mean a chemical reaction has occurred (Hofer, Mirwald, Bhasin, & Hofko, 2023; Nivitha, Prasad, & Krishnan, 2016). The shift in peak position (y-axis) can also be due to changes in intermolecular interactions.

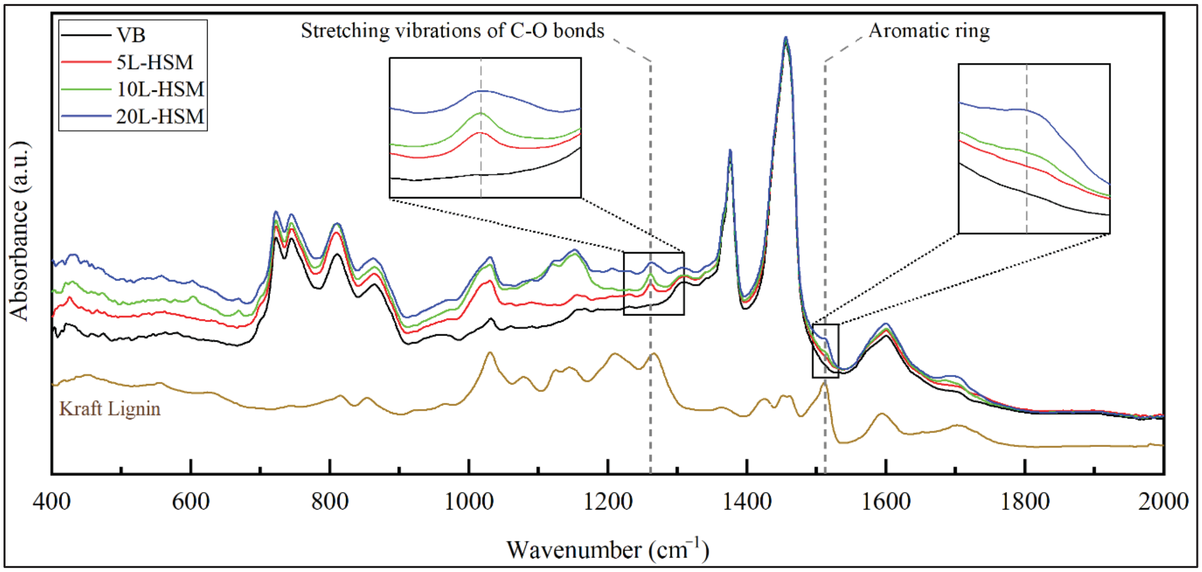


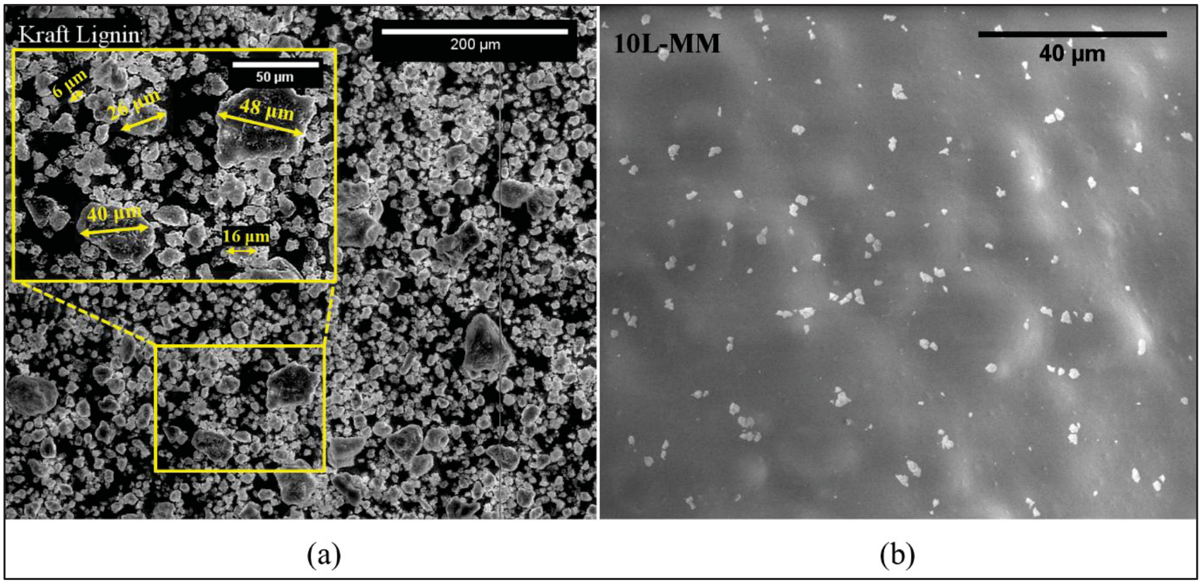
Figure 5.10 FTIR spectra of Kraft lignin, VB, 5L-HSM, 10L-HSM, and 20L-HSM samples (wavenumber of 400 to 2000 cm^{-1})

According to the test results, new peaks are generated at 2 wavenumbers of 1260 cm^{-1} and 1510 cm^{-1}, which intensified with increasing Kraft lignin percentage. The wavenumber of 1260 cm^{-1} is associated with the stretching vibration of C-O bonds in aliphatic and aromatic ethers, while the wavenumber of 1510 cm^{-1} is commonly attributed to the stretching vibration of aromatic ring structures (Nivitha et al., 2016). Meanwhile, Kraft lignin has peaks in the same wavenumbers, indicating the presence of Kraft lignin in the bitumen, not a new chemical reaction. On the other hand, the peak values of the curves for other wavenumbers are slightly different, but the peak positions of the curves are basically the same, indicating that the Kraft lignin does not produce new functional groups, but intensifies the existing peaks. It can be speculated that the physical interaction between the two components leads to the observed changes in the FTIR spectra, and no chemical reaction occurs. It is important to note that the FTIR results for the MM samples are consistent with those of the HSM samples, indicating that the blending conditions do not significantly affect the chemical composition of the modified bitumen. Based on these findings, it can be concluded that the addition of Kraft lignin to modified bitumen can alter the chemical structure of the bitumen without causing any chemical reaction between the two components. The results suggest an increase in the strength of certain chemical bonds due to the presence of Kraft lignin. These findings have important consequences for the use of Kraft lignin as a sustainable modifier for bitumen.

5.5.4 ESEM Results

Environmental Scanning Electron Microscopy (ESEM) was used to investigate the morphology of the Kraft lignin, virgin bitumen, and lignin-modified bitumen samples. To analyze the images, ImageJ software (version 1.52a) was used. The ESEM images provide valuable information about the microstructure, surface topography, and elemental composition of the samples.

Figure 5.11a shows a representative ESEM image of the Kraft lignin. The Kraft lignin particle sizes were analyzed using ESEM, and the results show that the particle sizes ranged from 2 to 50 μm. The particle size of Kraft lignin powder is a crucial factor that can influence the properties of lignin-modified bitumen. Smaller particle sizes promote uniform dispersion within the bitumen matrix, resulting in a homogeneous mixture. Additionally, smaller particles provide a larger interfacial area between lignin and bitumen, facilitating interaction and bonding. These findings are consistent with the observations from the laser granulometry test (Section 5.4.1.2 and Figure 5.2), indicating the reliability of the measurement methods employed. Moreover, the ESEM image reveals that the Kraft lignin particles exhibit angularity and rough surface characteristics. These features can be attributed to the inherent properties of Kraft lignin.



(a) (b)

Figure 5.11 ESEM image of: (a) Kraft lignin and (b) 10L-MM sample (magnification of ×1000)

Figure 5.11b shows the ESEM image of the Kraft lignin in bitumen for a 10L-MM sample. The visual observation of the sample reveals that there is a good dispersion of Kraft lignin in the bitumen, and there is no aggregation of Kraft lignin particles. The dispersion of Kraft lignin particles in bitumen is a crucial factor that can significantly affect the properties of the lignin-modified bitumen. A well-dispersed Kraft lignin powder can lead to improved performance properties. On the other hand, poor dispersion can lead to several negative effects, including reduced effectiveness of Kraft lignin, decreased homogeneity, and reduced mechanical properties of modified bitumen (Mansourian et al., 2019). The analysis of particle sizes shows that the visible particle sizes ranged 2 ± 1 μm. Interestingly, the measurement of the area shows that only 2.5 % of Kraft lignin is visible in the modified bitumen 10L-MM, suggesting that the remaining Kraft lignin (5.7 %) might have absorbed or dissolved in the bitumen (91.8 %)—here, percentage by volume, not by weight. To determine the percentage of visible Kraft lignin particles in the 10L-MM sample, a representative area was randomly selected for analysis. Individual particle areas were measured using ImageJ software.

Figure 5.12 shows nine ESEM images revealing the fibril (worm-shaped) structure of bitumen samples with three different percentages of Kraft lignin and two blending conditions. Upon examination of the images, it can be observed that the fibril structure of the bitumen samples is affected by both the Kraft lignin content and the blending conditions. Specifically, increasing the amount of Kraft lignin in the samples results in the more widespread distribution of visible Kraft lignin particles within the fibril structure, as shown in images c, d, e, g, h, and i (Figure 5.12). Furthermore, the blending process used during sample preparation also plays a crucial role in determining the fibril structure. Image b, which depicts virgin bitumen processed in a mechanical mixer (MM), exhibits a thinner diameter and more voids or pores in comparison to image f, showing virgin bitumen processed in a high-shear mixer (HSM). Based on the quantitative measurements, the average diameter of the fibril structure of the MM sample and HSM sample are 9.5 and 13.4 μm, respectively. The increased oxidation during blending using MM may have led to the thinner fibril structure observed. Based on the findings presented in this study, it can be concluded that both the Kraft lignin content and the blending conditions significantly affect the fibril structure of bitumen samples.

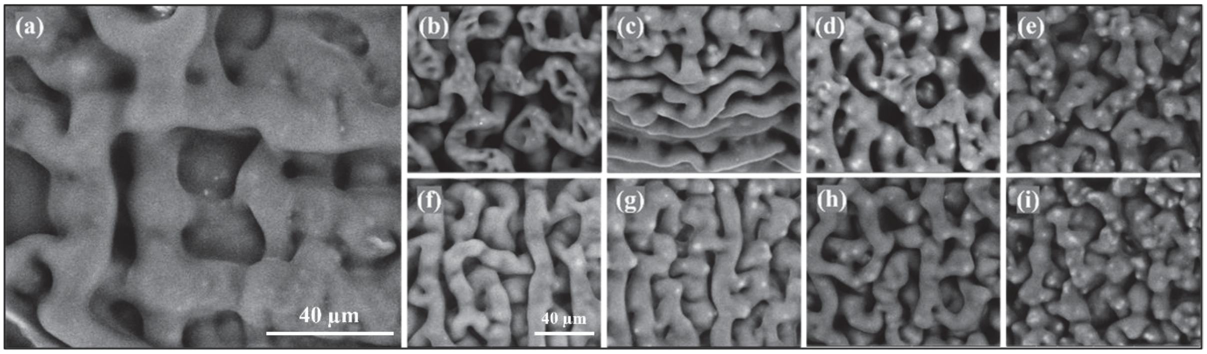


Figure 5.12 ESEM images for: (a) VB, (b) VB-MM, (c) 5L-MM, (d) 10L-MM, (e) 20L-MM, (f) VB-HSM, (g) 5L-HSM, (h) 10L-HSM, and (i) 20L-HSM

5.5.5 TGA Results

The thermal behavior of Kraft lignin and lignin-modified bitumen samples was studied using thermogravimetric analysis (TGA). This study aimed at evaluating the thermal characterization of Kraft lignin under combustion (thermal-oxidative) conditions and assessing the impact of Kraft lignin addition on the thermal behavior of bitumen within the operational temperature of the bitumen and hot mix asphalt. The TGA analysis was also carried out to evaluate the effect of blending conditions on the thermal behavior of the modified bitumen samples. The TG/DTG thermogram of Kraft lignin is shown in Figure 5.13.

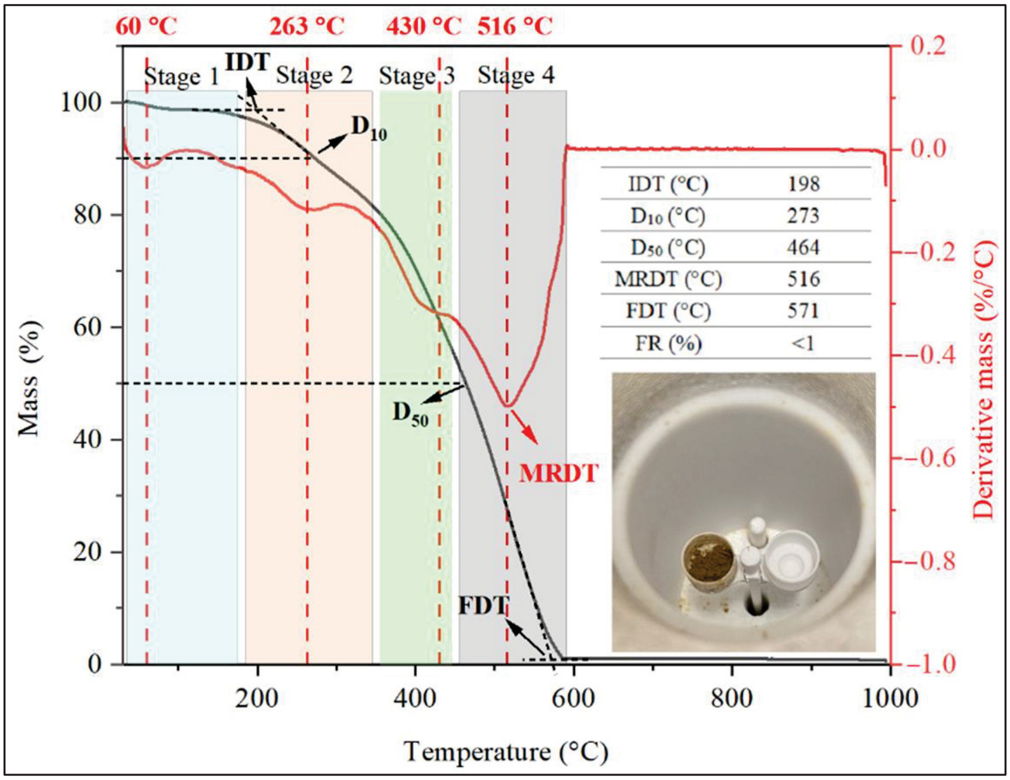


Figure 5.13 TG/DTG thermograms of Kraft lignin

The results show that Kraft lignin has an initial decomposition temperature (IDT) of 198 °C and a final decomposition temperature (FDT) of 571 °C. The D_{10} value, indicating 10 % decomposition of Kraft lignin, is 273 °C, while the D_{50} value, representing 50 % decomposition, is 464 °C. The weight loss process of Kraft lignin is divided into four (4) stages with respect to initial mass.

The 1st weight loss stage occurs at a temperature range between room temperature and 180 °C, caused by the dehydration drying process. This is due to the moisture that exists in the Kraft lignin. From room temperature to 100 °C, the weight loss is due to evaporation of free water. At 60 °C, the maximum weight loss rate is recorded. As the temperature rises, chemisorbed water begins to be removed (Jianfei et al., 2020; Saadatkhah et al., 2020). The weight loss for free and chemisorbed water is 1.3 and 2.6 %, respectively.

The 2nd weight loss stage takes place from 180 to 350 °C, where 16.4 % weight loss is observed due to thermal decomposition carbonization. During this stage, the polysaccharides and a small number of hydroxyl (-OH) and ether bonds (-C-O-C-) break down (Jianfei et al., 2020).

During the 3rd stage, which occurs within the temperature range of 350 to 450 °C, a weight loss of 26.3 % is observed. This stage involves the late phases of thermal decomposition and carbonization processes.

In the 4th stage, which takes place between 450 and 590 °C, a significant weight loss of 53.8 % is observed. This stage is characterized by the combustion of carbonized Kraft lignin. The release of these gases suggests that Kraft lignin is undergoing significant thermal degradation. The maximum rate of decomposition temperature (MRDT) of Kraft lignin is found at a temperature of 516 °C, which indicates the temperature range where the maximum component in the material is decomposing. The final residue (FR) of Kraft lignin is determined to be less than 1 %. The analysis of the TGA and DTG curves provides a clear understanding of the thermal behavior of Kraft lignin.

Thermal stability is an important property of bitumen, as it can affect its performance and durability. In this study, the thermal stability of the bitumen samples is evaluated. To quantify the thermal stability of the samples, the D_1 parameter is defined, which is the temperature at which 1 % of the sample decomposes. The D_1 values for all samples are determined from the TGA test results. The D_1 values provide valuable information on the thermal stability of the samples. A higher D_1 value indicates that the material is more thermally stable, as it can withstand higher temperatures before decomposing. Therefore, by comparing the D_1 values of the samples, the effectiveness of any modification processes on the thermal stability of the material can be evaluated.

As shown in Figure 5.14, the blending processes increase the D_1 value of the virgin bitumen (VB) from 242 to 265 °C for mechanical mixing (MM) and from 242 °C to 259 °C for high-shear mixing (HSM). The increase in the D_1 value of the VB-MM and VB-HSM suggests that the blending process may have improved the thermal stability of the material. The higher D_1 value indicates that the processed bitumen sample can withstand higher temperatures before decomposing, compared to the VB sample. VB-MM has a higher D_1 value in comparison to VB-HSM. The increase in the D_1 value could be attributed to the removal of volatile components and increased oxidation levels in the MM sample during the blending process, which can increase the molecular weight and stiffness and enhance resistance to thermal changes. Further investigation is required to fully understand the underlying mechanisms contributing to this observation.

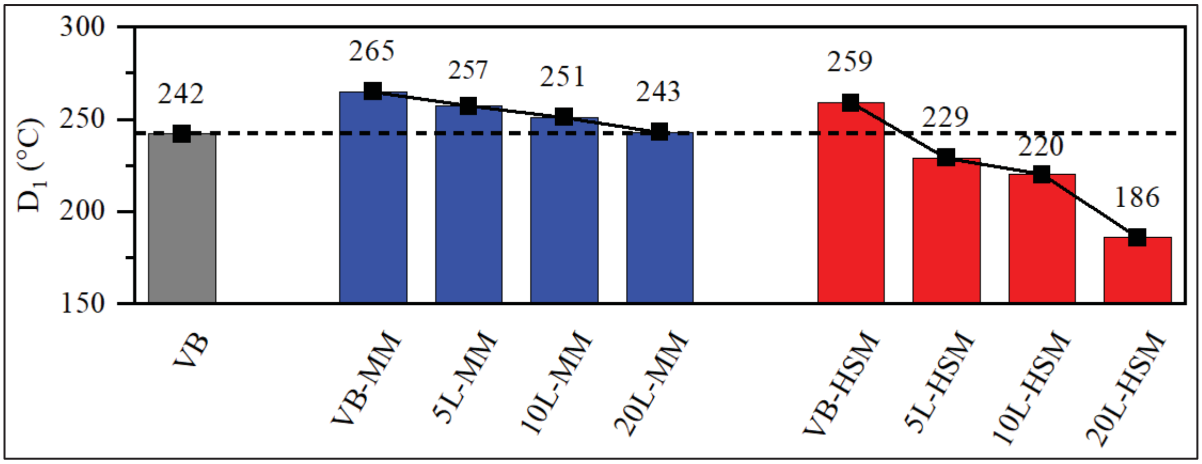


Figure 5.14 D_1 value of bitumen samples

The D_1 values for MM are 257 °C, 251 °C, and 243 °C for 5, 10, and 20 % of Kraft lignin, respectively. One of the reasons for the decrement in the D_1 value can be attributed to the lower thermal stability of Kraft lignin compared to bitumen. Moreover, the use of HSM results in a further decrease in thermal stability. The D_1 values for HSM samples are 229, 220, and 186 °C for 5, 10, and 20 % of Kraft lignin, respectively. Possible reasons for the lower thermal stability in lignin-modified bitumen samples include alterations to the chemical composition and microstructure of the bitumen, as well as the introduction of impurities or degradation during the Kraft lignin modification process. FTIR test results (Section 5.5.3) show no significant changes in functional groups, suggesting that chemical modifications to the bitumen are not the primary reason for the lower D_1 value. It is likely that multiple factors are contributing to the lower thermal stability of lignin-modified bitumen samples. Further investigation is required to determine the exact mechanisms involved.

The effect of different percentages of Kraft lignin on the operational temperature of the hot mix asphalt (<200 °C) was investigated by thermogravimetric analysis (TGA). The TG and DTG thermograms of the Kraft lignin, VB, and HSM samples are presented in Figure 5.15.

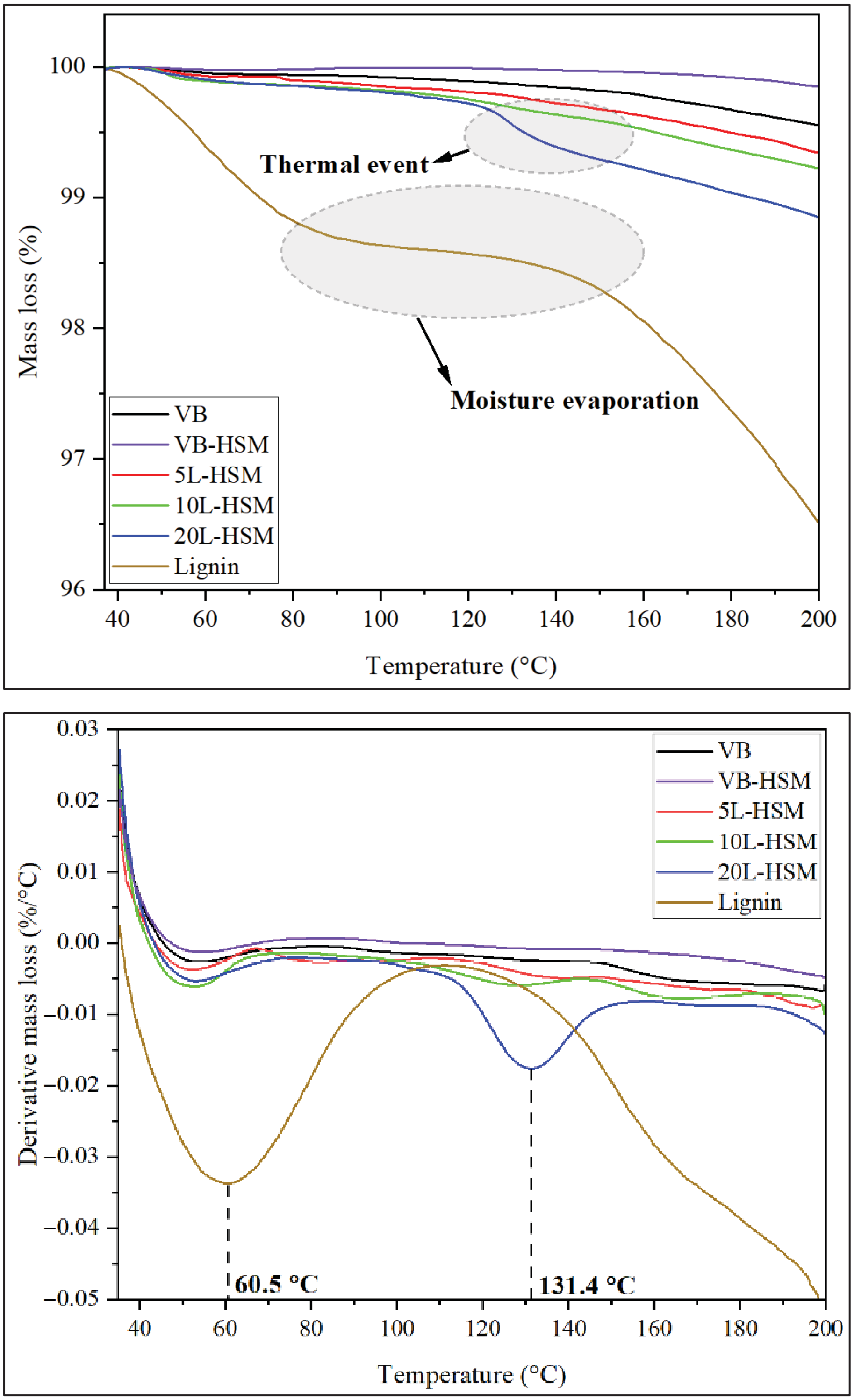


Figure 5.15 (a) TG and (b) DTG thermograms of VB, VB-HSM, 5L-HSM, 10L-HSM, and 20L-HSM samples on the operational temperature of the asphalt mix

The VB sample has more mass loss compared to the VB-HSM sample in the temperature range of 100–200 °C. This indicates that the blending process caused the loss of volatile components from the bitumen. The lignin-modified bitumen samples showed more mass loss than the VB and VB-HSM samples, and the mass loss increased with increasing Kraft lignin percentage. This result suggests that the presence of Kraft lignin in the bitumen affects its thermal behavior, which can be attributed to the thermal decomposition of Kraft lignin. Interestingly, a thermal event was observed at 131 °C in the 20L-HSM sample, which is not present in other samples. The reason for this thermal event is unclear, and further investigation is needed to understand the underlying mechanism. One possible explanation is that it could be related to the interaction between Kraft lignin and bitumen with a higher amount of Kraft lignin, leading to a new phase formation. Overall, the results prove that the addition of Kraft lignin to bitumen affects its thermal behavior, and the Kraft lignin percentage in the modified bitumen plays a significant role in determining the mass loss curve.

5.5.6 DSC Results

The glass transition temperature (T_g) and crystallinity are two (2) important parameters that can be determined from differential scanning calorimetry (DSC) test results of bitumen samples. Tg is the temperature at which the bitumen transitions from a glassy state to a rubbery state, and it can be determined from the onset of the slope change in the heat flow curve that occurs during heating. Crystallinity, on the other hand, is the measure of the degree of crystalline fraction in bitumen, and it can be determined by comparing the measured heat of fusion to the theoretical heat of fusion. These parameters are crucial for understanding the thermal properties of bitumen, which in turn can affect the performance of asphalt pavement. The effects of Kraft lignin modification and blending conditions on the thermal properties of bitumen are discussed by comparing the Tg and crystallinity values of all samples (Figure 5.16).

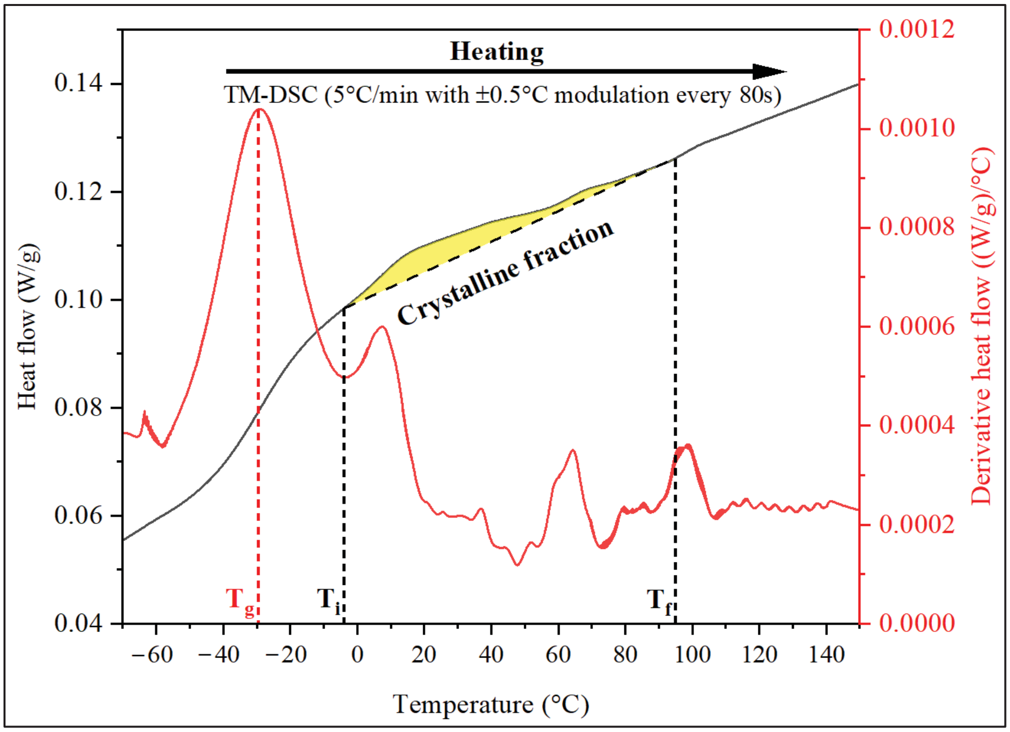


Figure 5.16 Glass transition temperature (T_g) and crystallization fraction of virgin bitumen using TM-DSC technique (T_i and T_f represent the initial and final temperatures, respectively, used to calculate the crystalline fraction)

As shown in Figure 5.17, the T_g values of the bitumen samples are obtained from the DSC analysis. In terms of blending conditions, it is observed that the T_g of the VB-HSM and VB-MM samples is −29.3, and −29.9 °C, respectively, which is lower than the VB sample (−29.2 °C). This suggests that the blending conditions have a small impact on the physical properties of bitumen.

In terms of the Kraft lignin effect, it is observed that the T_g of the HSM samples decreases as the Kraft lignin percentage increases, whereas the T_g of the MM samples remains relatively constant with increasing Kraft lignin content. This suggests that the effect of Kraft lignin on the T_g of bitumen is dependent on the blending conditions. The decrease in T_g with increasing Kraft lignin content in the HSM samples can be attributed to the increased interaction between the Kraft lignin and bitumen molecules due to the high shear rate. It is important to note that from the FTIR test results (Section 5.5.3), even if there is no chemical reaction between Kraft lignin and bitumen in HSM samples, the two components may still exhibit some degree of miscibility or compatibility with each other, which can also affect the Tg of the modified bitumen. It is important to acknowledge that the observed differences in Tg values among the samples are relatively small, within 1 °C. While these differences may not be as pronounced as in other studies (Fuentes-Audén et al., 2008; Peng Lin et al., 2021), they still provide valuable insights into the low-temperature behavior of modified bitumen.

In conclusion, the DSC analysis of the bitumen samples shows that the blending conditions and Kraft lignin content have a small, but positive impact on the glass transition temperature (T_g) of bitumen (lower values than VB). These results suggest that the incorporation of Kraft lignin in bitumen can be an effective method to modify the physical properties of bitumen, but the blending conditions must be carefully controlled to achieve the desired effect.

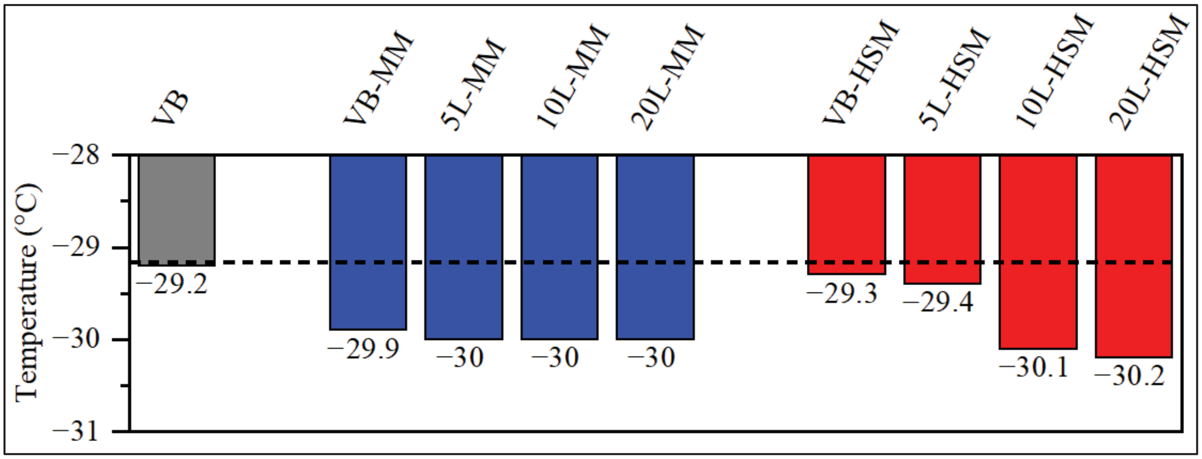


Figure 5.17 Glass transition temperature (T_g) of bitumen samples

The calculation of the crystallizable fraction (%) is performed to determine the content of the crystalline fraction in the VB and lignin-modified bitumen samples. Table 5.5 shows that there is not a significant change in the crystallizable fraction with the addition of Kraft lignin and blending conditions. A higher crystallizable fraction (yellow zone in Figure 5.16) indicates a greater degree of crystalline structure within the bitumen. In this study, despite the Kraft lignin modification, the crystallizable fraction remains relatively constant across the lignin-modified bitumen samples. This suggests that the addition of Kraft lignin does not have a substantial impact on the formation or content of the crystalline fraction within the bitumen. It is important to note that while the crystallizable fraction does not show significant changes, other thermal properties, such as the glass transition temperature (T_g), are influenced by the Kraft lignin addition and blending conditions, as discussed earlier. Further analysis and characterization techniques may be necessary to investigate the detailed effects of Kraft lignin modification on the crystalline structure of bitumen and its potential implications for the performance of asphalt pavement.

Table 5.5 Content of crystallizable fraction of samples

Code	Content of crystallizable fraction (%)
VB	1.4
VB-HSM	1.7
5L-HSM	1.5
10L-HSM	1.5
20L-HSM	1.4
VB-MM	1.6
5L-MM	1.5
10L-MM	1.4
20L-MM	1.2

5.6 Conclusions

In this study, the chemo-thermal characteristics of lignin-modified bitumen were investigated with different percentages (5, 10, and 20 %) of Kraft lignin under 2 blending protocols, including mechanical mixer (MM) and high-shear mixer (HSM). The results obtained from various tests, including Brookfield Rotational Viscosity (BRV), Dynamic Shear Rheometer (DSR), Fourier-Transform Infrared Spectroscopy (FTIR), Environmental Scanning Electron Microscopy (ESEM), Thermogravimetric Analysis (TGA), and Differential Scanning Calorimetry (DSC), provided valuable insights into the effect of blending conditions and properties of lignin-modified bitumen. The findings of the study are as follows. In terms of the influence of blending conditions:

- The MM-produced samples result in higher viscosity and |G*|/sin(δ) values compared to the HSM samples. Additionally, HSM samples exhibit distinctly different |G*| and δ values compared to the MM samples (Sections 5.5.1 and 5.5.2);
- The blending conditions do not significantly affect the chemical composition of the modified bitumen (Section 5.5.3); meanwhile, it affects the fibril structure of bitumen (Section 5.5.4);
- The thermal stability decreases more when using a HSM (Section 5.5.5);
- The T_g of HSM samples decreases with increasing Kraft lignin percentage, indicating an interaction between Kraft lignin and bitumen due to the high shear rate (Section 5.5.6).
- In terms of the Kraft lignin effect:
- The addition of Kraft lignin increases the viscosity, stiffness, high-temperature stability, and |G*|/sin(δ) value of bitumen (Sections 5.5.1 and 5.5.2);
- The addition of Kraft lignin alters the chemical structure of the modified bitumen without causing chemical reactions (Section 5.5.3). Moreover, increasing the amount of Kraft lignin in the samples leads to a more widespread distribution of Kraft lignin particles within the fibril structure, with no aggregation of Kraft lignin particles, here, for mass contents up to 20 % (Section 5.5.4);
- The addition of Kraft lignin to bitumen decreases the thermal stability. A thermal event observed at 131 °C in the 20L-HSM sample suggests a possible interaction between Kraft lignin and bitumen at higher Kraft lignin content (20 %), leading to the formation of a new phase (Section 5.5.5);
- The miscibility or compatibility between Kraft lignin and bitumen, even without chemical reaction, may slightly influence the T_g of modified bitumen, whereas the crystallizable fraction remains relatively constant across the lignin-modified bitumen samples (Section 5.5.6).

Finally, this study highlights the potential of Kraft lignin as a bitumen modifier and emphasizes the influence of blending protocols and Kraft lignin content on the performance and properties of lignin-modified bitumen. The choice of the mixer can have a significant impact on the quality and characteristics of the lignin-modified bitumen in terms of blending Kraft lignin with bitumen. While a mechanical mixer may be sufficient for some additives, a high-shear mixer can provide more consistent and higher-quality results for Kraft lignin. The findings contribute to the development of environmentally friendly approaches in the asphalt industry by utilizing waste materials as modifiers. Further research is required to optimize the blending process.

Further improvements can be made in the study of lignin-modified bitumen. It is essential to investigate TGA-FTIR, which provides a more comprehensive understanding of the chemical changes occurring during the thermal degradation process. To enhance future research in this area, considering additional analytical techniques are recommended, such as the determination of carbonyl and sulfoxide indices using FTIR, and the kinematic effect of lignin-modified bitumen through TGA. The results of this study are part of an ongoing effort and larger project to investigate the feasibility and performance of incorporating lignin into modified and unmodified bitumens, and cold, warm, and hot mix asphalts, and future publications will cover these aspects.

CHAPTER 6

LABORATORY STUDY ON SYNERGISTIC EFFECTS OF SASOBIT® ON RHEOLOGICAL AND CHEMO-THERMAL PROPERTIES OF LIGNIN-MODIFIED BITUMEN

Ali Rezazad Gohari[a], Sébastien Lamothe[a], Jean-Pascal Bilodeau[b], Ahmad Mansourian[c] and Alan Carter[a]

[a] Département de Génie de La Construction, École de Technologie Supérieure (ÉTS), 1100 Notre-Dame Ouest, Montréal, QC, Canada, H3C 1K3.
[b] Département de Génie Civil et de Génie Des Eaux, Université Laval, 1065 avenue de la Médecine, Québec, QC, Canada, G1V 0A6.
[c] Bitumen and Asphalt Department, Road, Housing and Urban Development Research Center, Marvi St., Farhangian St., Sheikh Fazlollah Highway, Tehran, Iran, P9Q8+99J.

Paper published in *International Journal of Road Materials and Pavement Design*, December 2024

6.1 Abstract

This laboratory study investigates the use of softwood Kraft lignin as a bitumen additive to reduce its environmental footprint and modify bitumen's properties. However, the lignin addition in bitumen can lead to some adverse effects, such as increased viscosity. Sasobit® was used to remedy those effects. This study evaluates the separate and synergistic effect of varying concentrations of Kraft lignin and Sasobit on the properties of bitumen. The chemo-thermal and rheological properties of the modified bitumens were investigated using the Fourier-transform infrared spectroscopy (FTIR) technique, thermogravimetric analysis (TGA), and Brookfield rotational viscometer (BRV), dynamic shear rheometer (DSR), multiple stress creep recovery (MSCR) and bending beam rheometer (BBR) tests. FTIR spectra demonstrate that no chemical reactions occur between additives and bitumen. Adding Sasobit increases the thermal stability of lignin-modified bitumen. Sasobit mitigates lignin-modified bitumen's viscosity. The Sasobit-lignin combination enhances bitumen's rutting resistance and viscoelastic properties, but adversely affects the low-temperature performance.

Keywords: Softwood Kraft lignin; Sasobit; lignin-modified bitumen; rheological properties; chemo-thermal properties; bitumen additive.

6.2 Introduction

Transportation infrastructures are essential for the smooth functioning of modern societies, connecting communities and supporting economic growth (Samli, 2010). Asphalt pavements are a fundamental aspect of this infrastructure, playing a significant role in ensuring effective, safe, and reliable transportation. The construction of asphalt pavements traditionally relies on bitumen as the binder. The sustainability of these pavements is crucial, not just for their longevity and performance under traffic and weather conditions, but also for their environmental impact. As the global focus moves towards sustainable development, enhancing the environmental friendliness of asphalt pavements has become imperative. This involves not only the adaptation of existing materials and techniques but also the development of innovative approaches to pavement construction that are both durable and environmentally friendly (Pouranian & Shishehbor, 2019; Sha et al., 2021). To address these challenges, this study investigates sustainable materials such as Kraft lignin and Sasobit as bitumen additives, evaluating their potential to reduce environmental impact and enhance pavement performance.

6.3 Background

6.3.1 Bitumen

Bitumen is used as a low-cost viscoelastic material, required to be resistant to climate and traffic loads. Bitumen requires specific physical and rheological properties, as it should flow easily for proper mixing while remaining stiff enough in hot weather to prevent rutting and soft and elastic at low temperatures to resist thermal cracking. From a chemical point of view, bitumen is mainly composed of a complex mixture of hydrocarbons and their derivatives, which generally exhibit a reduction in viscosity when heated. However, the exact mechanisms governing these changes are complex and involve multiple factors, including bitumen's chemical structure and the interactions between its constituent molecules (Lesueur, 2009; Mirwald et al., 2022). Despite its widespread use and importance, there are challenges associated with the use of bitumen in its current form, including its environmental impact and the need for improved durability and performance. To enhance bitumen's performance, a variety of additives have been employed successfully, such as polymers, chemical modifiers, organic modifiers, and nano-materials (Mansourian et al., 2019; Porto et al., 2019). There has been a growing interest in the use of sustainable alternatives and additives that can enhance the properties of bitumen, thereby improving the overall performance and sustainability of asphalt pavements.

6.3.1.1 Lignins and Kraft lignin additive for bitumen

One such material that has gained considerable attention is lignin (Bruijnincx et al., 2016; Pérez, Pasandín, Pais, & Pereira, 2019; Xie et al., 2017). Lignin is a renewable, affordable, and non-toxic material that has become prominent in the asphalt industry as an additive or alternative extender for bitumen and asphalt mix (Feldman et al., 1986; J. Wu et al., 2021).

Of all the lignins, Kraft lignin is an organic substance derived from the production of Kraft paper that can be made from softwood or hardwood and has a range of potential applications due to its chemical composition and physical properties (Kouisni, Gagné, Maki, Holt-Hindle, & Paleologou, 2016). Notably, Kraft lignin has chemical attributes that enable it to act effectively as a free radical scavenger, enhancing the resilience of asphalt binders as an antioxidant (Adwani et al., 2023). Research studies have focused on the different properties of lignin-modified bitumen, investigating how various types of lignin additives with different percentages affect viscosity, aging, high and low-temperature performances, chemical interactions, and thermal properties (Gao et al., 2020; Kalampokis et al., 2022; Y. Li et al., 2023; Pasandín et al., 2022; Su et al., 2023; C. Xu et al., 2021; Y. Zhang et al., 2019; Y. Zhang et al., 2022). Generally, Kraft lignin addition reduces the performance at low temperatures (higher stiffness and lower creep relaxation), but it improves the performance at intermediates, high and very high temperatures (higher: viscosity; complex shear modulus; stability; resilient modulus; water, fatigue and rutting resistance) of bitumen or mix (Arafat et al., 2019; Gao et al., 2020; Hobson, 2017; Lamothe, Carret, Al-Falahat, & Carter, 2022; Lynam, Wasiuddin, Arafat, Kumar, & Owhe, 2018; Poeran, 2014; Ren et al., 2021; Sundstrom, Klei, & Daubenspeck, 1983; J. Wu et al., 2021; Xie et al., 2017; C. Xu et al., 2021; G. Xu et al., 2017; Zahedi, Zarei, & Zarei, 2020; R. Zhang, Sun, et al., 2021; Y. Zhang, Wang, et al., 2020).

Despite the potential benefits, the incorporation of Kraft lignin into bitumen presents specific challenges that need to be addressed to fully realise its potential as a sustainable additive. One of the first primary challenges associated with the use of Kraft lignin in bitumen is the increased viscosity of lignin-modified bitumens (Al-falahat et al., 2024). Our recently published research study has been crucial in addressing this issue (Rezazad Gohari, Lamothe, Bilodeau, Mansourian, & Carter, 2023). The study was part of a larger project to investigate the feasibility of adding softwood Kraft lignin into a variety of bitumens and asphalt mixes and the performance of those mixes. In that study, we investigated the chemo-thermal properties of lignin-modified bitumen by employing two distinct blending protocols to evaluate its performance as an additive and the effect of blending conditions on its performance. Based on our study, we observed that as the percentage of Kraft lignin increases, the viscosity of the bitumen increases. With the same compaction energy, the higher viscosity of lignin-modified bitumen can have negative effects on the asphalt mixes, including an increase in the air voids content, otherwise, it is necessary to increase the mixing and compaction temperatures to avoid this, which is undesirable from an environmental point of view. This issue requires the development of innovative solutions that can mitigate this challenge and ensure the successful application of Kraft lignin in asphalt pavements.

6.3.2 Warm mix asphalt (WMA)

Warm mix asphalt (WMA) is a technology that allows the production and compaction of asphalt mixes at lower temperatures compared to traditional hot mix asphalt (HMA) (Sukhija & Saboo, 2021). This reduction in temperature which can vary approximately between 20 and

40 °C depending on the additive and technology leads to significant energy savings. This technology involves the use of specific additives or mechanisms that enable asphalt mixes to be processed at these lower temperatures without compromising the pavement's performance. There are different types of WMA technologies, such as organic additives, chemical additives, foaming technologies, and hybrids, which aid in achieving the desired asphalt properties at lower temperatures (Mansoori & Modarres, 2020). Each of these additives plays a unique role in improving the workability, compactability, and performance of asphalt mixes (Cheraghian et al., 2020). But, among various WMA additives, including Cecabase RT® and Rediset WMX®, Sasobit® was found to be the most effective in improving workability and enhancing the stiffness modulus of bitumen at intermediate and high temperatures, making it a suitable solution for paving in hot weather conditions (Bilema et al., 2023). Additionally, Sasobit demonstrated better performance at low temperatures compared to Evotherm, further enhancing its value as an additive (B. Hu, Ai, & Feng, 2024).

6.3.2.1 Sasobit® additive for WMA

Sasobit® is a widely used organic WMA additive, with numerous studies conducted on its application. Sasobit is distinct from the usual waxes found in bitumen, as it is manufactured through the Fischer–Tropsch polymerisation process (Hurley & Prowell, 2005). Sasobit can be incorporated into the asphalt mix using two primary methods. In the wet process, the additive is blended directly with the bitumen. In the dry process, the additive is mixed with the aggregate and bitumen during asphalt mix production (Sampath, 2010). Sasobit has a melting point of approximately 100 °C and becomes completely soluble in asphalt binder at temperatures exceeding 120 °C. Consequently, waxes act as softeners at very high temperatures, at mixing and compaction temperatures, affecting the binder's performance (or viscosity) (Edwards & Redelius, 2003). Its application in the asphalt industry is growing due to its ability to enhance workability and provide significant benefits, such as reduced energy consumption and pollutant emissions and lower mixing and compaction temperatures by approximately up to 40 °C (Fazaeli, Amini, Nejad, & Behbahani, 2016). Sasobit is well known as a bitumen flow enhancer, helping to reduce the viscosity of the bitumen. Studies have consistently shown that Sasobit effectively decreases the viscosity of bitumen, particularly when used at a concentration of 3 % (Ghuzlan & Al Assi, 2017; Köse, Çelik, & Arslan, 2024).

An interesting area of research involves combining Sasobit with other additives to leverage their specific properties and achieve desired performance characteristics. For example, integrating polymer-modified bitumen (PmB) with Sasobit has shown improved workability without compromising performance, despite the challenges posed by the opposing effects on viscosity and stiffness (Akisetty, Gandhi, et al., 2010; Akisetty, Lee, et al., 2010; Edwards et al., 2010; Rossi, Filippi, Merusi, Giuliani, & Polacco, 2013). For instance, in a study where Sasobit was added to a linear low-density polyethylene (LLDPE) asphalt mixture, the reduction in viscosity led to decreased energy consumption and enhanced thermo-oxidative aging resistance (Tembe et al., 2023). Gong et al. also demonstrated that Sasobit significantly reduces the viscosity of epoxy SBS-modified asphalt (ESBA) (Gong et al., 2020). Similarly, Wu et al. found that incorporating Sasobit into Styrene–butadiene rubber-modified asphalt (SBRMA) at a 4 % concentration effectively lowered the mixture temperature by 14 °C (D. Wu, Zhao, Peng, Cheng, & Zhou, 2023). Sasobit has also been shown to enhance the high-temperature stability of bitumen and improve resistance to decomposition (Tembe et al., 2023; D. Wu et al., 2023; Yue, Yue, Wang, Guo, & Ma, 2023).

When the temperature drops below its melting point (100 °C), waxes or Sasobit act more as fillers and form a crystalline network structure within the bitumen, which enhances bitumen stiffness and permanent deformation resistance and maintains its crystalline structure at in-service temperatures of pavement (Hurley & Prowell, 2005). Sasobit has been found to enhance the resistance to rutting at elevated temperatures (Ghuzlan & Al Assi, 2017; Köse et al., 2024). Its addition increases the complex modulus, decreases the phase angle (δ), and improves the high-temperature stability of the bitumen (Yue et al., 2023). Liu et al. investigated a unique composition involving 5, 10, 15, and 20 % Buton rock asphalt (BRA) with 3 % Sasobit in virgin bitumen. The resulting Buton rock asphalt composite modified warm mix asphalt (BCMWMA), revealed that the modification process was mainly physical, with no changes observed in the chemical structure of the modified bitumen (W. Liu et al., 2023). Its ability to improve high-temperature performance makes it a valuable additive in asphalt applications where such performance is critical. At intermediate temperatures, the addition of Sasobit does not significantly alter the binder's performance against fatigue cracking (Ghuzlan & Al Assi, 2017). Sasobit has been observed to negatively affect the performance of asphalt binder at lower temperatures (Ghuzlan & Al Assi, 2017; Tembe et al., 2023). In particular, it should be noted that the incorporation of Sasobit should never exceed 4 % by the weight of the bitumen to avoid negatively affecting the bitumen's low-temperature properties (Edwards & Isacsson, 2005; Hainin et al., 2015; Jamshidi, Hamzah, & You, 2013).

In summary, the use of sustainable additives such as Kraft lignin in bitumen for asphalt pavements holds significant promise for improving the performance, durability, and sustainability of transportation infrastructure. However, the challenges associated with the increased viscosity of lignin-modified bitumen must be addressed to fully realise the potential benefits of this approach. Sasobit has emerged as a potential solution to these challenges, with previous studies demonstrating its effectiveness in reducing the viscosity of bitumen modified with lignin or other additives such as polymers.

6.4 Objective and scope

Kraft lignin being a sustainable additive in bitumen for asphalt pavements, this laboratory study particularly focuses on evaluating the effect of Sasobit on the properties of lignin-modified bitumen. More specifically, this investigation evaluates Sasobit's effectiveness in mitigating the increased viscosity and other adverse effects caused by introducing Kraft lignin into bitumen. To achieve this, the study investigates the introduction of Sasobit as an additional additive to counteract these negative effects. The scope of the research is to evaluate the separate and synergistic effect of varying concentrations of Kraft lignin and Sasobit on the properties of bitumen. Specifically, the study focuses on: (1) Investigating the chemical interaction and thermal properties using Fourier-transform infrared spectroscopy (FTIR) technique and thermogravimetric analysis (TGA); (2) Assessing the viscosity changes and the mixing and compaction temperatures through the Brookfield rotational viscometer (BRV) test;

(3) Examining the viscoelastic properties and rutting potential using the dynamic shear rheometer (DSR) test; (4) Assessing high-temperature performance using the multiple stress creep recovery (MSCR) test and; (5) Investigating the low-temperature performance through the bending beam rheometer (BBR) test.

While the primary focus of the current research study is on the rheological properties of bitumen, which are directly linked to pavement performance, the introduction of Sasobit and Kraft lignin necessitates a thorough investigation of chemo-thermal properties as well. Changes in the chemical structure and thermal behavior of modified bitumen, although not directly impacting pavement performance, are crucial. Through this targeted analysis, the research will determine the effectiveness of Sasobit in mitigating the adverse effects of softwood Kraft lignin on bitumen properties and establish guidelines for the effective use of these materials. The outcome will contribute to a more sustainable and durable infrastructure by integrating softwood Kraft lignin into asphalt mixtures.

6.5 Laboratory experimental program

6.5.1 Materials

6.5.1.1 Bitumen

In this study, an unmodified PG 58S−28 bitumen, adapted for cold climate (−28 to 58 °C) and standard (S) traffic level, tested and supplied by Bitumar in Canada was utilised. This unmodified bitumen is also tested by us and referred to as virgin bitumen (VB) in this study. The technical specifications of the bitumen, as provided by the manufacturer’s data sheet, include a flashpoint of 273 °C (ASTM D 92), a density of 1.021 g/cm^3 at 25 °C (AASHTO T 228), and Brookfield viscosities of 309 mPa·s at 135 °C and 92 mPa·s at 165 °C (AASHTO T 316). The storage stability is 0.3 °C (LC 25-003), the ash content is 0.28 % (ASTM D 8078), and the $|G^*|/\sin(\delta)$ value at 58 °C is 1.54 kPa (AASHTO T 315).

6.5.1.2 Softwood Kraft lignin

The softwood Kraft lignin employed in this study was sourced from FPInnovations in Canada and utilised in our previous laboratory study (Rezazad Gohari et al., 2023). This specific Kraft lignin type is derived using the LignoForce™ technology co-developed by FPInnovations and NORAM (Suota et al., 2021). This technology emphasises the extraction and purification of Lignin from black liquor, a byproduct of the Kraft pulping process essential to paper production. Through a specialised sequence of oxidation and acidification, Lignin is precipitated out, then washed and dewatered to yield a highly purified product (Kouisni et al., 2016). The Kraft lignin was obtained in the form of a sticky brown fine powder derived from softwood (Figure 6.1a). The unique properties of this Kraft lignin make it ideal for this study. Its properties, as provided by the supplier, include a density that ranges from 1.2 to 1.3 g/cm3. The potential hydrogen (pH) of this lignin is between 3 and 4, and its molecular weight is reported 5185 g/mol. The moisture content of the lignin is relatively low, between 1 and 2 %, and was determined using an oven according to the CAN/BNQ 2501–170 standard. Further details on the physical properties of Kraft lignin, such as particle size distribution and thermal behavior, are discussed in our previously published paper (Rezazad Gohari et al., 2023).

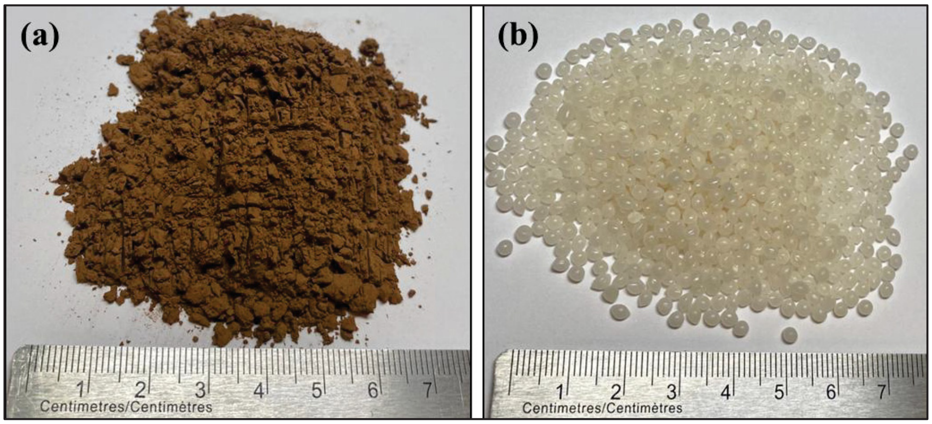


Figure 6.1 (a) Kraft lignin powder and (b) Sasobit prills

6.5.1.3 Sasobit

Sasobit, as a warm mix asphalt additive, is an organic additive produced by Sasol wax company in South Africa (Figure 6.1b). It comprises long-chain hydrocarbons that are derived from the coal gasification process (SasolChemicals, 2025). Because of the existing body of literature, two Sasobit concentrations were chosen for this study, which are 1 and 3 % by weight of the lignin-modified bitumen (Jamshidi, Hamzah, & You, 2013). Moreover, according to the producer's recommendation, the optimal results are achieved with a 3 % addition of Sasobit, by weight of bitumen, which can effectively lower the maximum temperature by 30 °C for asphalt mix (SasolChemicals, 2025). Table 6.1 shows the properties of Sasobit.

Table 6.1 Properties of the Sasobit used in this study (provided by the supplier)

Properties (unit)	Value
Penetration at 25 °C (0.1 mm)	1
Penetration at 65 °C (0.1 mm)	8
Melting point (°C)	100
Flashpoint (°C)	290
Potential hydrogen (pH value)	Neutral (7)
Density (kg/m^3)	590
Brookfield viscosity at 135 °C (mPa·s)	12
Color	White to yellowish
Physical State	Pills (No odor)

6.5.2 Sample Preparation

In this study, Kraft lignin and Sasobit additives were blended with the virgin bitumen in different percentages using the wet process. Weight percentages of 0, 1, and 3 % Sasobit and 0, 5, 10, and 20 % Kraft lignin, as well as combinations of these percentages, were selected resulting in the formation of 13 distinct samples (Table 6.2). It is important to note that all samples for FTIR technique, TG analysis (TGA), and DSR test are unaged. Aging processes, including the rolling thin film oven test (RTFOT) and the pressure aging vessel (PAV), were employed for MSCR and BBR tests. Kraft lignin's concentrations were selected based on the fact that, for this type of Kraft lignin, the maximum percentage to maintain stability and homogeneity in the bitumen is 30 % (Al-falahat et al., 2024). Therefore, these percentages were chosen to ensure optimal stability and uniformity in the lignin-modified bitumen samples. For a deeper understanding of the intrinsic effect of the blending process, virgin bitumen (VB) was subjected to the same blending (or mixing: M) protocol without introducing Kraft lignin and Sasobit. This sample is designated as VBM. Table 6.2 presents the details of each sample, including the percentage of Kraft lignin and Sasobit added, and the corresponding sample code.

Table 6.2 Composition details and naming of additives with bitumen

Sample composition	Kraft lignin (wt %)[1]	Sasobit (wt %)[2]	Sample (code)
Virgin Bitumen (VB)	0	0	VB
			VBM[3]
Virgin Bitumen (VB) with added Sasobit (S)	0	1	1S
		3	3S
Lignin-modified bitumen (L) with added Sasobit (S)	5	0	5L
		1	5L1S
		3	5L3S
	10	0	10L
		1	10L1S
		3	10L3S
	20	0	20L
		1	20L1S
		3	20L3S

[1] The Kraft lignin content is a percentage of the total weight of the lignin-modified bitumen (Kraft lignin + bitumen).

[2] The Sasobit content is a percentage of lignin-modified bitumen.

[3] Virgin bitumen processed in blending (or mixing) protocol without additives.

The blending of Kraft lignin, Sasobit, and bitumen in an oil bath using a high-shear mixer is illustrated in Figure 6.2. The oil bath was used to provide uniform heating from all sides, ensuring that the bitumen and additives were exposed to consistent temperatures during blending. Although specific heating molds designed for this purpose exist, the oil bath system was chosen based on the availability of equipment at the time of the study. This approach ensured the necessary temperature control for the blending process. The step-by-step sample preparation and blending protocol are comprehensively outlined in Figure 6.3. The blending was conducted at a controlled temperature of 150 ± 5 °C. It is important to note that blending temperature can influence the final properties of the bitumen-additive mixture (Shafii, Veng, Rais, & Ab Latif, 2017). Initially, the virgin bitumen (VB) was placed in an oven for 1 hour at 150 °C to ensure it reached the proper temperature. Afterward, the bitumen was placed in an oil bath for 20 minutes to equilibrate the temperature before the blending process began. As the temperature equilibrated, the blending process was initiated, and the additives were gradually added over 15 minutes. For the samples with both Kraft lignin and Sasobit, Sasobit was added first to decrease the viscosity of the bitumen, followed by the addition of Kraft lignin to ensure better mixing. The blending was performed at a constant speed of 5,000 rpm, utilising a Silverson L4RT high-shear mixer. Based on the findings of our previous research, a high-shear mixer (HSM) was preferred to a mechanical mixer (MM), given its proven efficacy with lignin-modified bitumen, while limiting evaporation, oxidation, and increased bitumen viscosity (Rezazad Gohari et al., 2023). Subsequently, the oil bath was adjusted to 140 °C to compensate for the temperature rise caused by the high-shear mixer. Blending was continued at 5,000 rpm for an additional 45 minutes.

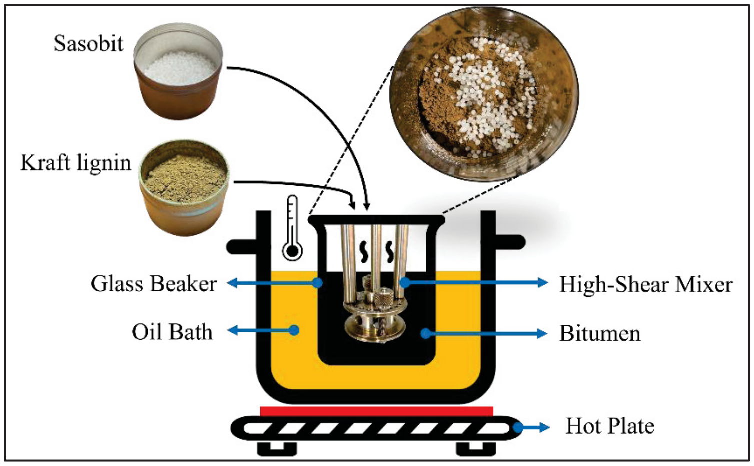


Figure 6.2 Blending Kraft lignin, Sasobit, and bitumen in an oil bath using a high-shear mixer

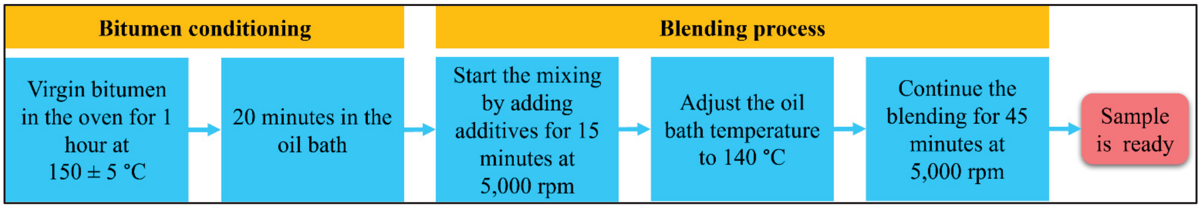


Figure 6.3 Steps of the blending process

6.5.3 Testing methodology

Following the flowchart depicted in Figure 6.4, the experimental plan was designed to ensure a thorough evaluation of the samples. Once the samples were prepared, the chemo-thermal properties of the samples were analyzed through the Fourier-transform infrared spectroscopy (FTIR) technique and thermogravimetric analysis (TGA). In parallel, their rheological properties were assessed using the Brookfield rotational viscometer (BRV), dynamic shear rheometer (DSR), multiple stress creep recovery (MSCR), and bending beam rheometer (BBR) tests. At least two replicates were conducted for all tests to provide an indication of variability, and all replicates were within the acceptable range specified by the relevant laboratory standards.

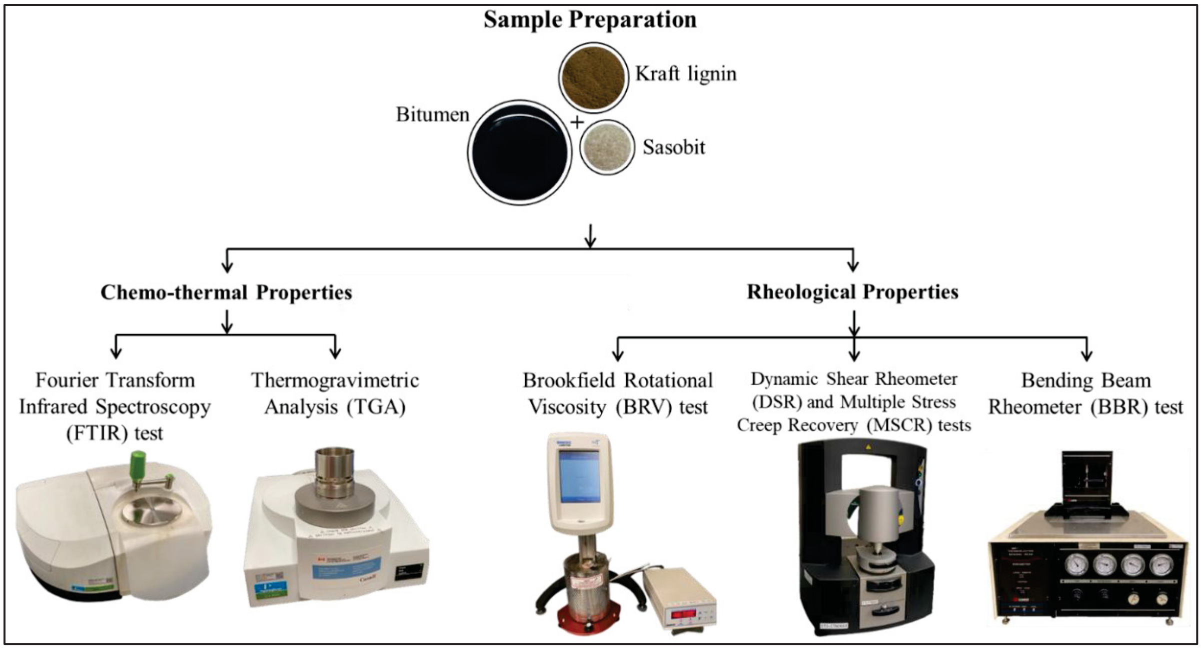


Figure 6.4 Flowchart of the experimental plan

6.5.4 Determination of chemo-thermal and rheological properties

6.5.4.1 Fourier-transform infrared spectroscopy (FTIR) technique

FTIR spectroscopy is a critical method utilised to detect and monitor changes in the molecular and chemical compositions of bitumen. The attenuated total reflectance (ATR)-FTIR method was employed for this study. A notable characteristic of this method is its specificity to the molecular compounds present on the sample's surface. As a result, it can be used for testing viscous and liquid nature samples, such as bitumen, thereby eliminating the need for complex preparations (Mirwald et al., 2022). In this study, the Spectrum Two™ FTIR Perkin Elmer was employed, which was equipped with a Diamond ATR crystal. The measurements were performed over a wavenumber range from 400 to 4000 cm^{-1} with a resolution set at 4 cm^{-1}. For each spectrum, a total of 20 scans were recorded. To prepare the samples, 2–3 g of bitumen sample was poured on oil paper as a droplet. After cooling to room temperature (23 °C), the sample was placed on the measurement crystal and pressed gently to ensure good contact. Such close contact amplifies the signal detected by the FTIR spectrometer. Before testing, the crystal was cleaned with limonene and isopropanol, and a background spectrum was captured to ensure accurate readings.

6.5.4.2 Thermogravimetric analysis (TGA)

TGA is a thermal analysis technique used to determine the thermal properties of materials and changes in weight in relation to temperature or time. In this study, for all samples, approximately 20 mg of homogenised sample was weighed and placed in a ceramic pan. The TGA instrument was calibrated as per manufacturer guidelines and the tests were performed over a temperature range from room temperature to 1,000 °C (intermediate to extreme temperature), increasing at 10 °C/min. A consistent gas flow of 50 mL/min was maintained. Kraft lignin powder was analyzed under both air and nitrogen (N_2) gas atmosphere, while bitumen and Sasobit samples were tested in an air atmosphere. Throughout the heating process, the instrument continuously recorded the sample's weight, allowing the determination of weight percentage against temperature.

6.5.4.3 Brookfield rotational viscometer (BRV) test

The viscosity is a crucial parameter that quantifies the resistance of bitumen to flow under applied stress. Bitumen viscosity significantly influences workability and rheological behavior during the mixing, compaction, and application phases. Furthermore, an optimal viscosity is critical for ensuring adequate aggregate coating in asphalt mixes, which directly affects the durability, moisture resistance, and overall performance of the asphalt mix. When Kraft lignin and Sasobit additives are added to bitumen, they can substantially alter its viscosity. Consequently, an accurate viscosity measurement is essential for ensuring the desired performance and durability of asphalt mixes (Hunter et al., 2015). Viscosity can be accurately determined using the BRV test. A Brookfield DV2 T viscometer was used for viscosity measurements at 135, 145, 155, and 165 °C for all samples using the LC 25–007 Quebec test method (LC: *Laboratoire des chaussées*) of the Ministère des Transports et de la Mobilité Durable (MTMD).

6.5.4.4 Dynamic shear rheometer (DSR) test

To evaluate the linear viscoelastic (LVE) properties of the unaged bitumen samples modified with Kraft lignin and Sasobit, the DSR test plays a significant role. In this study, the DSR test was conducted to thoroughly investigate these properties, according to the AASHTO T315 standard. The DSR test was conducted at three distinct temperatures of 58, 64, and 70 °C at an angular frequency of 10 rad/s (1.59 Hz). In this test, a thin bitumen sample, sandwiched between two parallel plates of the rheometer, was subjected to oscillatory shear stress, with the resulting strain measured. A sinusoidal shear load was applied at a frequency of 10 rad/s using a plate with a diameter of 25 mm and a bitumen thickness of 1 mm. From these measurements, key rheological parameters, including the norm of the complex shear modulus ($|G^*|$) and the phase angle (δ), were derived. These parameters are essential in understanding the effect of additives on the modified bitumen's behavior. Additionally, to assess the rutting resistance potential of the bitumen samples, the $|G^*|/\sin(\delta)$ values were calculated and analyzed.

6.5.4.5 Multiple stress creep recovery (MSCR) test

The MSCR test is an advanced rheological testing method defined by AASHTO T 350 standard which is incorporated into the 4101 standard of the MTMD of Quebec, designed to evaluate the rutting resistance of bitumen. Before testing, bitumen samples are aged to simulate the effects of short-term aging using the rolling thin-film oven (RTFO) test according to AASHTO T 240 standard. The MSCR test employs a cyclic loading method. Each bitumen sample is subjected to a one-second creep load, followed by a nine-second recovery phase. This process was conducted at two stress levels of 0.1 and 3.2 kPa over ten cycles each, at temperatures of 52, 58, and 64 °C. Nonrecoverable creep compliance derived from the MSCR test is a good indicator of the permanent deformation resistance of the modified bitumen under cyclic loading.

6.5.4.6 Bending beam rheometer (BBR) test

To evaluate the low-temperature properties of asphalt binders, the bending beam rheometer (BBR) test is conducted according to AASHTO T 313 standard following two aging processes. Initially, the bitumen samples were aged through the rolling thin film oven (RTFO) and pressurised aging vessel (PAV) tests, which simulate short-term and long-term aging, respectively. Following aging, a bitumen beam of $6.35 \times 12.7 \times 127 \text{ mm}^3$, is subjected to a low-temperature environment using a bending-beam rheometer device. During the test, a 980 ± 50 mN load is centrally applied to the bitumen beam, to measure midpoint deflection. The creep stiffness of the sample is calculated at 8, 15, 30, 60, 120, and 240 s after the load application begins. Equation 6.1 used for calculating the stiffness of the asphalt binder at any given time t is given by:

$$S(t) = \frac{PL^3}{4bh^3\delta(t)} \qquad \text{Equation 6.1}$$

where $S(t)$ represents the stiffness at time t, P is the load applied, L is the distance between the supports, b is the width of the beam, h is the thickness of the beam, and $\delta(t)$ is the deflection at time t. Additionally, the m-value (creep relaxation), which indicates the rate of stiffness change over time, is specifically calculated at the loading time of 60 s. The m(60) alongside the creep stiffness modulus, S(60), is crucial for assessing the asphalt's potential to resist thermal cracking at temperatures lower than the specified low-temperature (L) grade. An S(60) value below 300 MPa and an m(60) above 0.3 are indicative of satisfactory performance against thermal cracking. Given the potential adverse low temperature effects of Sasobit and lignin on the modified bitumen, monitoring these criteria becomes more essential.

6.6 Results and Discussion

6.6.1 FTIR results

FTIR is used as a crucial tool to investigate the molecular interactions of Sasobit and Kraft lignin with bitumen, shedding light on the chemical and physical alterations within the modified bitumen. To maintain uniformity and enable comparison, all spectra were normalised using the min–max normalisation method (Mirwald et al., 2022). In the FTIR spectra, all absorbance values are presented in arbitrary units (a.u.), which serve as a relative measure of the absorption intensity at various wavenumbers (cm^{-1}). This study investigates the individual effects of Sasobit and Kraft lignin on bitumen, as well as the synergistic effect of both additives.

Figure 6.5 shows FTIR of VB, 1S, 3S, and the pure Sasobit. Sasobit exhibits distinct FTIR peaks representing its unique molecular structure. The peaks at 719 cm^{-1} and 730 cm^{-1} are indicative of aromatic compounds. Vibrations denoted by 1462 cm^{-1} represent CH_2 scissoring/bending, while 1473 cm^{-1} characterises CH_3 asymmetric and symmetric bending. Peaks at 2848 cm^{-1} and 2915 cm^{-1} relate to CH_2 asymmetric stretching and CH_3 asymmetric stretching, respectively (Y. Chen et al., 2015). By adding Sasobit to bitumen with two concentrations, 1 and 3 %, the FTIR spectra display no formation of new peaks. Meanwhile, the positions of peaks remained unaltered, evidencing no lateral shifts. This consistent positioning and the absence of new peaks suggest that no chemical reactions are observed by the introduction of Sasobit into the bitumen. Furthermore, a distinct trend is observed in the FTIR analysis. The addition of Sasobit, to the bitumen results in a reduction in the absorbance intensity of specific peaks in the spectrum, as illustrated by the detailed view provided in Figure 6.5. From a molecular point of view, bitumen comprises a complex mixture of hydrocarbons with a diverse range of functional groups (Hunter et al., 2015). Each of these groups contributes to the FTIR spectrum based on its concentration, leading to peaks of varying absorbance intensities. Sasobit primarily consists of long-chain alkanes with fewer and less diverse functional groups compared to the bitumen, its addition results in a reduction of the overall functional group density in the modified mixture. This effect has a direct consequence on the FTIR spectrum. A decrease in the functional group density due to the addition of Sasobit leads to a proportional reduction in the absorbance intensity of the corresponding peaks (Sobhi, Hesami, Poursoltani, Ayar, & Mullapudi, 2022).

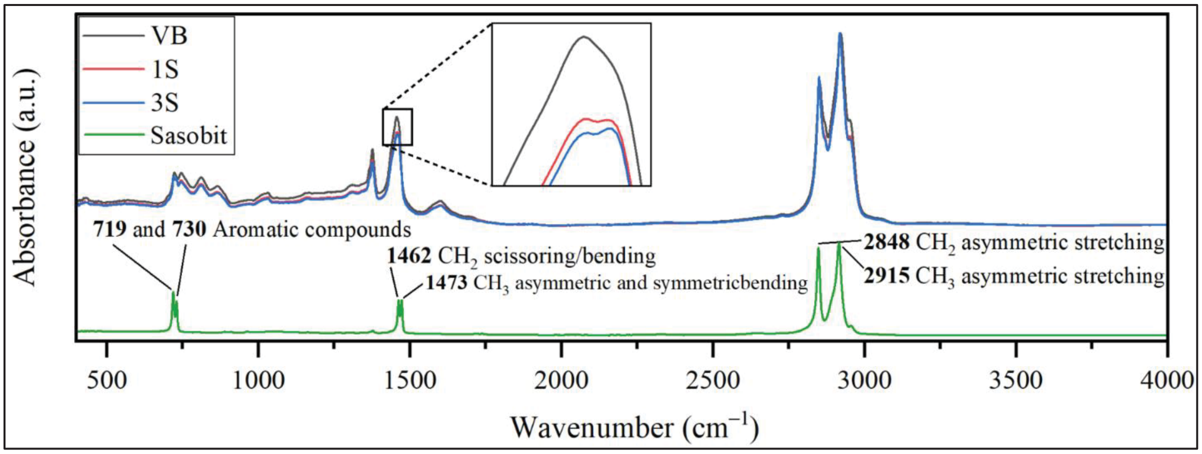


Figure 6.5 FTIR spectra of Sasobit, VB, 1S, and 3S samples (wavenumber 400 to 4000 cm $^{-1}$)

Figure 6.6 presents the FTIR spectra of VB, 5L, 10L, 20L, and pure Kraft lignin samples. Kraft lignin, a complex organic polymer, shows distinct FTIR peaks reflective of its molecular composition. In the 1500–1650 cm^{-1} range, peaks correspond to C–H and C=C bond vibrations in phenolic compounds, highlighting the aromatic nature of Kraft lignin. The wavenumber of 1218–1268 cm^{-1} indicates the presence of C–O stretching bonds, a common bond in lignin. Absorbance in the 1030–1080 cm^{-1} range correlates to ether intermolecular C–O–C bond vibrations. Additionally, peaks at 2937 cm–1 and 2833 cm–1 align with vibrations of the methoxy –OCH3 group in Lignin (Boeriu, Bravo, Gosselink, & van Dam, 2004; Kalampokis et al., 2022). The addition of Kraft lignin to bitumen, as observed in the 5L, 10L, and 20L samples, does not lead to the formation of any new peaks in the FTIR spectra (Figure 6.6). This consistent observation across the spectra suggests that the integration of Kraft lignin into the bitumen does not induce chemical reactions, a finding that aligns with our previous research study (Rezazad Gohari et al., 2023). However, certain regions of the spectra (between 400 and 1350 cm^{-1}) reveal an increase in absorbance in the lignin-modified bitumen samples, which are shown in the enlarged section of Figure 6.6. This suggests that there is an enhanced presence or concentration of specific functional groups, or possibly heightened intermolecular interactions, influenced by the softwood Kraft lignin.

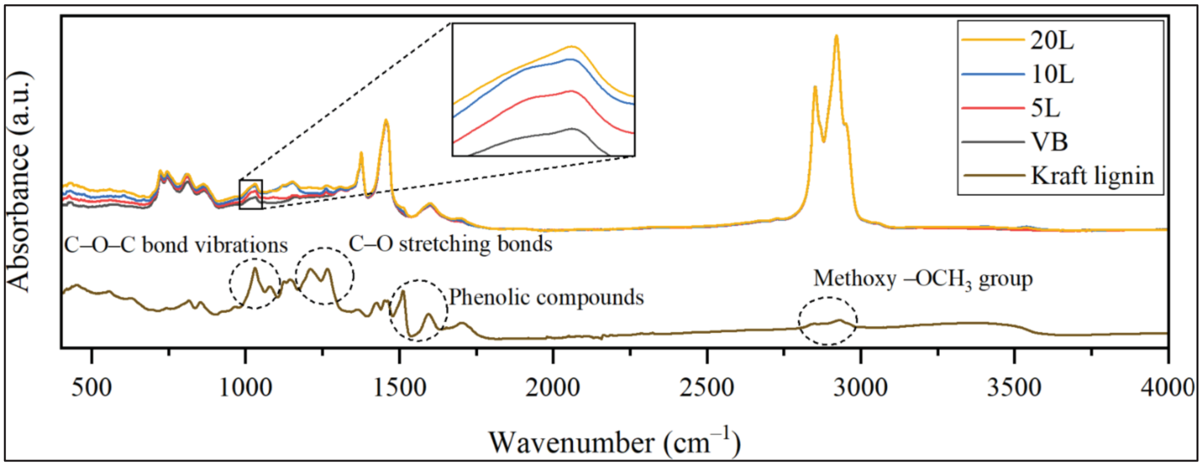


Figure 6.6 FTIR spectra of Kraft lignin, VB, 5L, 10L, and 20L samples (wavenumber: 400 to 4000 cm $^{-1}$)

Figure 6.7 illustrates the FTIR spectra of selected samples including VB, 5L3S, 10L3S, 20L3S, Sasobit, and Kraft lignin. Both Kraft lignin and Sasobit, individually identified as organic compounds, present distinct FTIR peaks that highlight their unique molecular configurations. When these two additives are blended with bitumen in different percentages, the resultant spectra for the 5L3S, 10L3S, and 20L3S samples do not reveal the formation of any new peaks (Figure 6.7). This spectral consistency strongly implies that no chemical reactions occur by the incorporation of both Kraft lignin and Sasobit into the bitumen. However, variations in the absorbance intensities at specific wavenumbers in the modified bitumen samples provide evidence of their presence. These changes in absorbance indicate the synergistic effect of the additives on the bitumen's molecular structure as shown by the detailed view provided in Figure 6.7. The increased or decreased absorbance levels can be attributed to the physical distribution and interactions of the added Kraft lignin and Sasobit within the bitumen, rather than any chemical modifications. The results demonstrate the significance of physical interactions over chemical reactions in shaping the spectral properties of the modified bitumen.

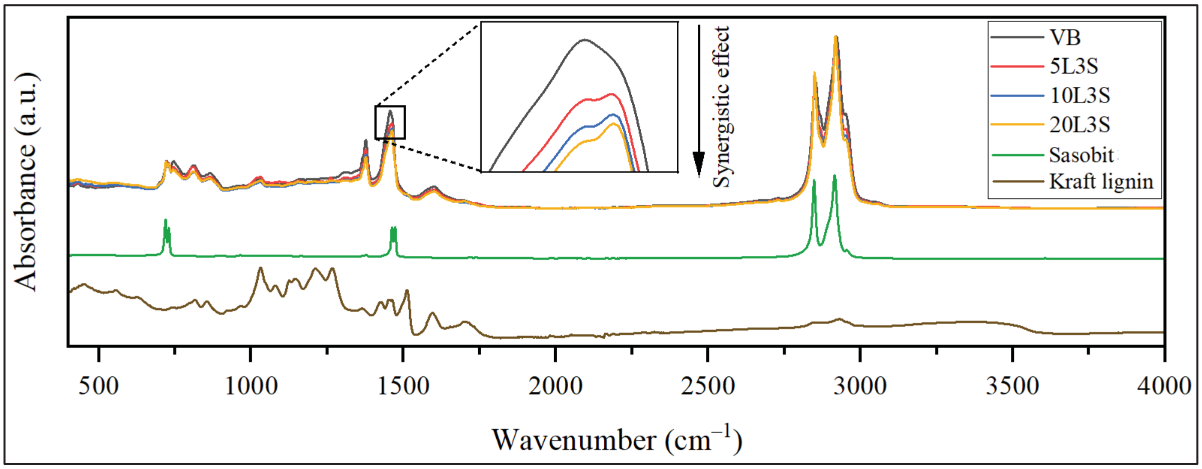


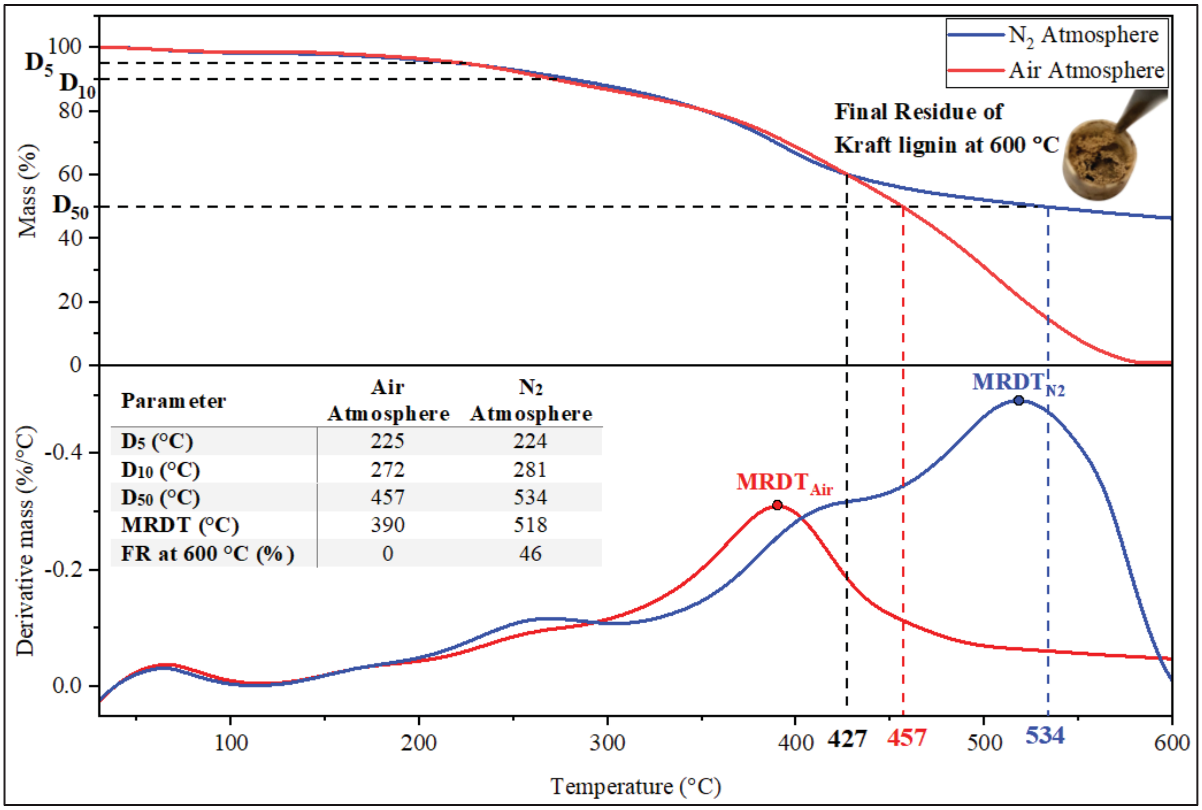
Figure 6.7 FTIR spectra of VB, Kraft lignin, Sasobit, 5L3S, 10L3S, and 20L3S samples (wavenumber of 400 to 4000 cm^{-1})

6.6.2 TGA results

The thermal behavior, from intermediate to extreme temperature, of Kraft lignin, Sasobit, and all bitumen samples were investigated using TGA. To ensure consistent and reliable results, each sample was tested twice. Also, TGA can be conducted under various atmospheres, each influencing the degradation behavior of the sample differently. Two common atmospheres include air, which introduces oxidative processes, and nitrogen (N_2) which provides an inert environment conducive to pyrolysis. The choice of the atmosphere is crucial, as it determines the decomposition process and resultant thermal pattern observed during TGA.

Initially, Kraft lignin was analyzed in both atmospheres to perform a comparative analysis of the thermal behavior. The presence of oxygen in the air can facilitate oxidative degradation of the sample, where the Kraft lignin undergoes processes similar to combustion, resulting in the release of volatile products such as CO and CO_2. In contrast, under N_2 atmosphere, oxidative processes are eliminated since N_2 is an inert gas. Therefore, the decomposition observed mainly stems from the thermal breakdown of the organic structure of the Kraft lignin. This process can be entirely different from the one observed under oxidative conditions and can lead to the formation of a distinct set of degradation products.

Figure 6.8 presents the TG/DTG thermograms of Kraft lignin under both air and N_2 atmospheres. The initial stages of thermal decomposition are often characterised by D_5 and D_{10} parameters. D_5 represents the temperature at which 5 % of the sample has decomposed, while D_{10} indicates the temperature at which 10 % decomposition is observed. In this study, these values show very slight differences between the two atmospheres. The D_5 value under the air atmosphere is 225 °C, while for N_2, it is 224 °C. Furthermore, the D_{10} values for the two atmospheres were observed at 272 and 281 °C, respectively. These results indicate the similarity in initial decomposition patterns under both conditions. However, these parallel decomposition pathways start to separate after reaching 427 °C, a point where 40 % of Kraft lignin decomposition is observed. Beyond this temperature, the thermal behavior of Kraft lignin in the two atmospheres exhibits noticeable differences. A significant difference is observed in the D_{50} value, indicating the temperature at which 50 % of the Kraft lignin has decomposed. For air, the D_{50} value is 457 °C, whereas, under the N_2 atmosphere, it is noticeably higher at 534 °C. The maximum rate of decomposition temperature (MRDT) for air is observed at 390 °C. In comparison, under the N_2 atmosphere, the MRDT is recorded at 518 °C, reflecting a different degradation rate. The TGA reveals one of the most significant differences between the two atmospheres. In an air atmosphere, the Kraft lignin is fully degraded, leaving no residue. However, under N_2, 46 % of the sample, represented as the final residue (FR), remains un-degraded even at 600 °C. In conclusion, while the initial degradation stages of Kraft lignin under both air and N_2 atmospheres are almost identical, subsequent stages reveal different thermal behaviors. This demonstrates the importance of considering the choice of the atmosphere in TGA testing, especially when evaluating Kraft lignin which exhibits different decomposition patterns.



Parameter	Air Atmosphere	N$_2$ Atmosphere
D$_5$ (°C)	225	224
D$_{10}$ (°C)	272	281
D$_{50}$ (°C)	457	534
MRDT (°C)	390	518
FR at 600 °C (%)	0	46

Figure 6.8 Thermograms of Kraft lignin under air and nitrogen (N$_2$) atmosphere

In terms of the operational temperature of asphalt mix, at a very high temperature but < 200 °C, TGA is employed to understand the thermal properties of bitumen when modified with Kraft lignin and Sasobit additives, separately. The results of these analyses are illustrated in Figure 6.9 and Figure 6.10, respectively.

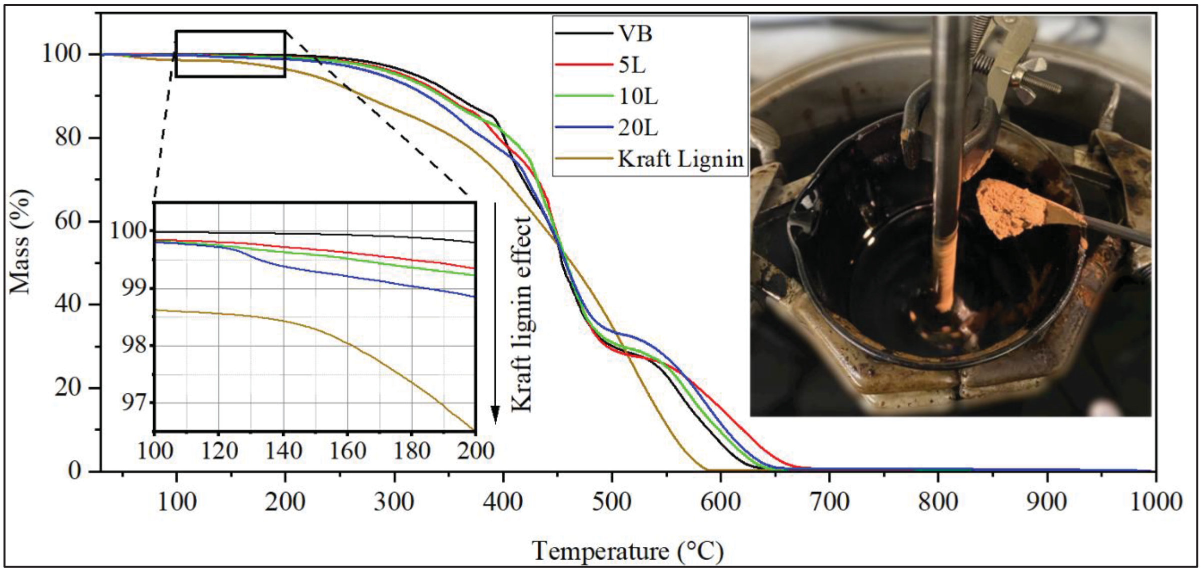


Figure 6.9 Thermograms of VB, 5L, 10L, 20L, and Kraft lignin samples

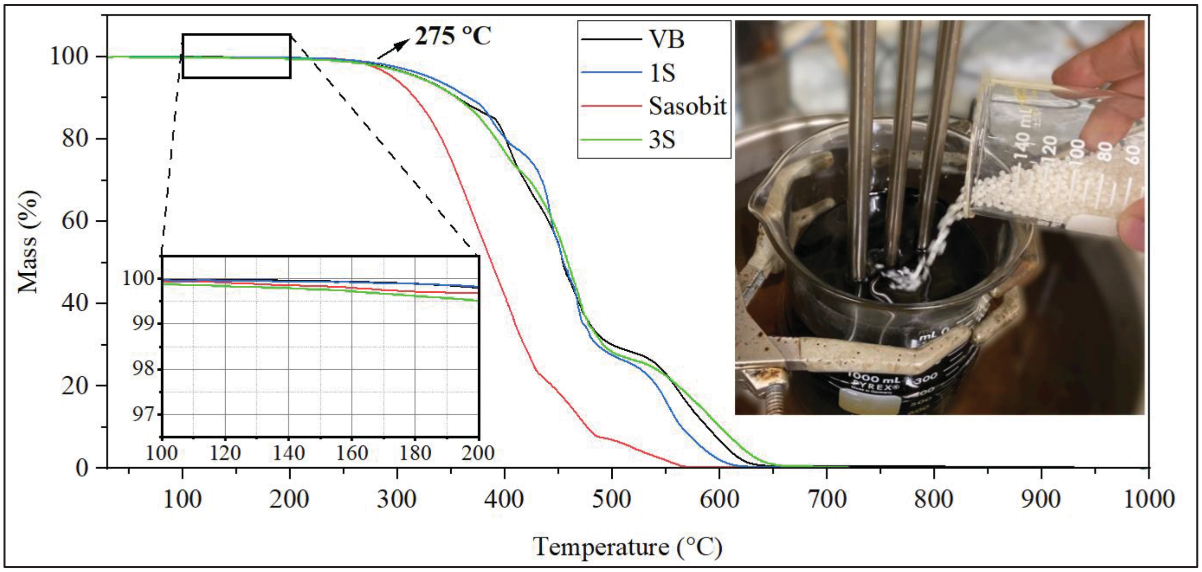


Figure 6.10 Thermograms of VB, 1S, 3S, and Sasobit samples

Figure 6.9 shows thermograms of five samples including VB, 5L, 10L, 20L, and pure Kraft lignin. A significant insight from the Kraft lignin thermogram is the moisture evaporation, leading to 1.5 % mass loss at 100 °C. Moreover, Kraft lignin exhibits a notably higher mass loss when compared to virgin bitumen, a difference attributed to the inherent properties and chemical composition of Kraft lignin. As the Kraft lignin percentage in bitumen increases, a consistent growth in mass loss is observed. When Kraft lignin is added to bitumen, in the operational temperature of asphalt mix (< 200 °C), a greater proportion of lignin-modified bitumen degrades in comparison to virgin bitumen (VB). This observation indicates that in the asphalt mix design, the thermal degradation of lignin-modified bitumen with a 20 % lignin concentration leads to a quantifiable loss of mass. Specifically, the decomposition of 1 % of the lignin-modified bitumen in the operational temperature of the asphalt mix results in a reduction in the bituminous content. To compensate for this loss and maintain the mix's desired properties for its intended application, it is essential to adjust the mix design by increasing the bitumen content proportionally. This adjustment ensures that the asphalt mix retains its performance characteristics throughout its service life. In summary, Kraft lignin influences negatively the thermal behavior of lignin-modified bitumen.

Figure 6.10 presents thermograms for VB, 1S, 3S, and pure Sasobit. Sasobit's thermal behavior differs from virgin bitumen, specifically after 275 °C. Within the operational temperature range of asphalt mixtures (< 200 °C), the introduction of 1 and 3 % Sasobit to virgin bitumen has a negligible effect on the thermal behavior of bitumen.

The thermal behavior of bitumen is fundamental to its performance, particularly at elevated temperatures. Rapid weight loss in bitumen upon thermal exposure may indicate susceptibility to evaporation of the lightweight portion, premature aging, increased hardening, and accelerated degradation, which can affect pavement performance. In this laboratory study, specific thermal parameters are defined to investigate the thermal stability of all bitumen samples. The objective is to investigate the effect of each additive as well as the synergistic effects on the thermal stability of bitumen. To quantify the thermal stability of the sample, three parameters are defined including D_1, D_5, and D_{10} (Figure 6.11b) which represent the temperature at which 1, 5, and 10 % of the sample decompose, respectively. The reason for selecting three distinct decomposition percentages is to consider that only 1 % weight loss (D_1) may be susceptible to impurities or lignin moisture. Hence, by integrating D_5 and D_{10} alongside D_1, a more robust and reliable insight into the sample's thermal behavior is achieved. Additionally, to provide a more comprehensive analysis, the D_{50} and MRDT parameters are also considered (Figure 6.11a). These parameters further validate the thermal stability assessment. A higher value for any of the parameters indicates enhanced thermal stability, as bitumen samples can withstand higher temperatures before undergoing the specified levels of decomposition.

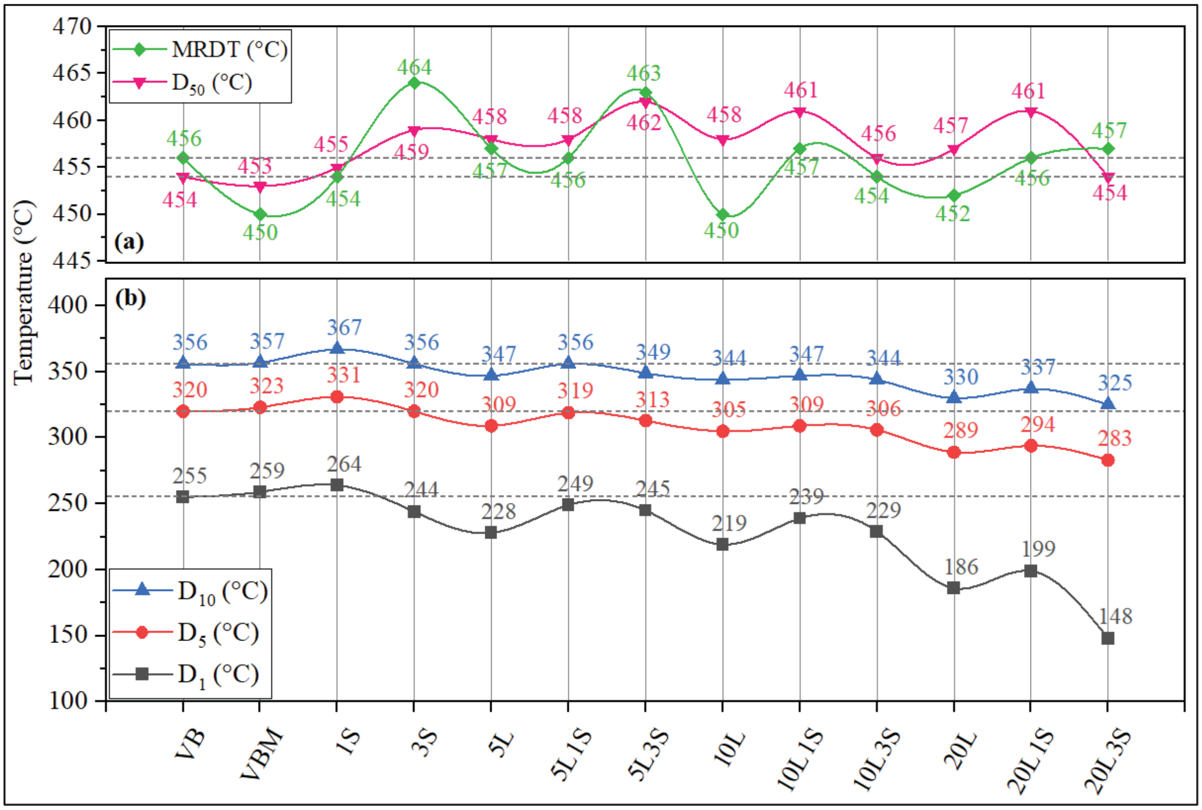


Figure 6.11 Thermal parameters of the bitumen samples: (a) MRDT and D_{50} and, (b) D_{10}, D_5, and D_1

Figure 6.11 presents the thermal parameters of the bitumen samples obtained from the TGA. Test results indicate that the blending process has a slight influence on the thermal stability of bitumen. For instance, the D_{10} value shows an increase of just 1 °C, changing from 356 °C for the VB sample to 357 °C for the VBM sample.

The addition of Sasobit influences the thermal stability of bitumen. With a 1 % Sasobit inclusion, the D_{10} value increases from 356 °C for the VB sample to 367 °C. At low concentrations, Sasobit may delay bitumen's initial degradation. In contrast, a higher Sasobit content (3 %) results in a D_{10} value shifting back to 356 °C. While a 1 % concentration of Sasobit enhances thermal stability, increasing the concentration to 3 % introduces negative interactions that neutralise these benefits, leading to no observable enhancement in thermal stability.

Kraft lignin significantly affects the thermal stability of bitumen. By adding 5, 10, and 20 % Kraft lignin, the D_{10} value decreases from 356 °C for the VB sample to 347, 344, and 330 °C for 5L, 10L, and 20L samples, respectively (Figure 6.11b). This trend can be attributed to Kraft lignin's properties degrading faster than bitumen. Hence, a higher Kraft lignin content decreases the modified bitumen's thermal stability further, which is not desirable for bitumen performance.

The effect of adding Sasobit to lignin-modified bitumen is similar to its effect on virgin bitumen. In case of Figure 6.11b, the addition of 1 % Sasobit increases the D_{10} values for 5, 10, and 20 % lignin-modified bitumen from 347, 344, and 330 °C to 356, 347, and 337 °C, respectively. Furthermore, an increase in the Sasobit concentration to 3 % leads to a reduction in thermal stability in comparison to the lignin-modified bitumen with 1 % Sasobit, however, it remains an enhancement over the pure lignin-modified bitumen. The results for D_1 and D_5 parameters confirm the trends noted for D_{10}, providing further validity to the results. When examining the D_{50} and MRDT values, the trends generally align with those of the lower decomposition temperatures. However, given that these values represent higher temperature behaviors, some irregularities are observed.

According to the TGA results, it's observable that the 5L1S sample exhibits almost identical thermal stability to the VB sample. This relation suggests an optimal Sasobit and Kraft lignin blend in the 5L1S sample based on thermal stability. The significance of these findings is heightened when considering the complex nature of bitumen modification using various additives. Each additive introduces unique molecular interactions, altering the thermal stability of the final product. This phenomenon highlights the importance of monitoring mass loss behaviors, especially when these are indicative of potential volatile or organic compounds or changes in viscoelastic properties.

6.6.3 BRV results

Viscosity variations for all bitumen samples at 135, 145, 155, and 165 °C (at very high temperatures) are illustrated in Figure 6.12. These results represent the effect of the mixing process, Kraft lignin, and Sasobit additives, as well as the synergistic effect of these additives on virgin bitumen (VB). The measured viscosities contribute to understanding the distinct effects of these additives on the viscosity of the bitumen. Analysis of the results confirms a clear effect of the mixing (M) process on the viscosity of bitumen without any additives. The viscosity values for the VB and VBM samples are 303 and 331 mPa·s at 135 °C, respectively. This indicates an 9 % increase in viscosity that is related solely to the mixing process. It is noteworthy that, as demonstrated in our previous study (Rezazad Gohari et al., 2023), the use of a mechanical mixer (MM) during the mixing process further increases the viscosity, as shown in the diagram labelled as VBM*. This highlights the significant role of the mixing process in determining bitumen's final viscosity.

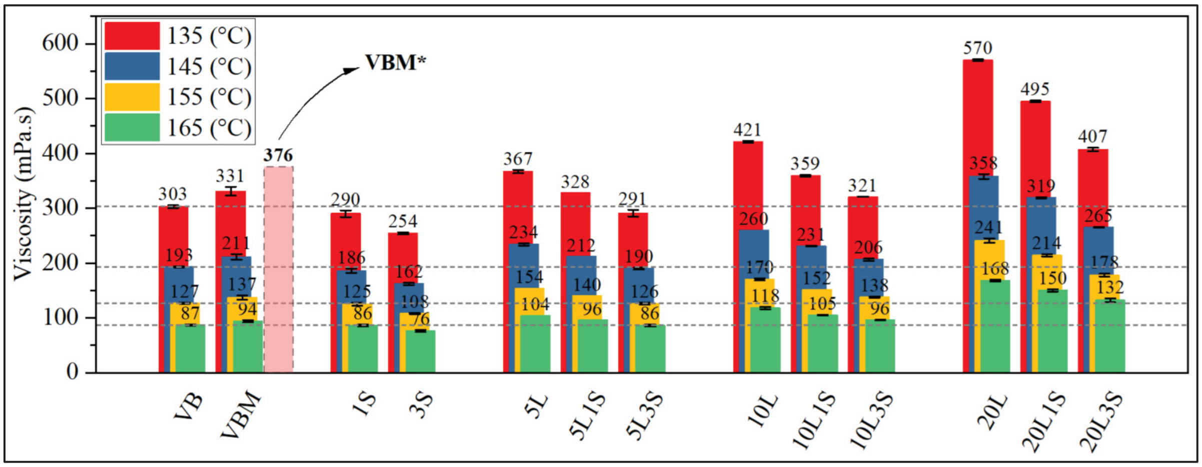


Figure 6.12 The viscosity of bitumen samples at 135, 145, 155 and 165 °C (error bars based on two replicates)

The addition of Sasobit to bitumen decreases its viscosity. At 135 °C, the viscosity values for VB, 1S, and 3S samples are 303, 290, and 254 mPa·s, respectively. The incorporation of 1 % Sasobit results in a minor decrease of approximately 3 % in viscosity across all tested temperatures. However, the most significant effect on viscosity is observed with the addition of 3 % Sasobit, resulting in a notable reduction of around 14 %. This considerable reduction demonstrates the efficiency of Sasobit in decreasing the viscosity of the bitumen. The observed viscosity reduction can be attributed to the properties of Sasobit. Sasobit, being a wax-based additive, significantly modifies the bitumen's internal microstructure. This restructuring is mainly attributed to the dispersion of Sasobit's long-chain aliphatic hydrocarbons within the bitumen. Moreover, the linear molecular chains of Sasobit disrupt the inherent interactions among the bitumen molecules. This disruption facilitates a diminished resistance to shear, leading to a decrease in viscosity (Qin et al., 2014).

However, adding Kraft lignin to bitumen distinctly increases its viscosity. Viscosity measurements at 135 °C for the VB, 5L, 10L, and 20L samples are 303, 367, 421, and 570 mPa·s, respectively. As Kraft lignin content increases in the bitumen, viscosity increases as well, as was observed in the research by Al-falahat et al. (Al-falahat et al., 2024). The incorporation of 5, 10, and 20 % of Kraft lignin increases the viscosity up to 21, 36, and 89 %, respectively. The possible mechanisms behind this significant viscosity increment are due to several factors. Firstly, Kraft lignin's molecular weight is higher than typical bitumens, increasing the overall viscosity of the mixture (C. Xu et al., 2021). Secondly, the inherent polarity of both bitumen and Kraft lignin intensifies the rheological properties and causes additional interactions and complexities within the bitumen's structure when combined (Ren et al., 2021). Lastly, the powdered form of Kraft lignin introduces solid particles into the bitumen, further increasing its resistance to flow (Al-falahat et al., 2024).

Upon evaluating the synergistic effects of the viscosity of Kraft lignin and Sasobit on bitumen, interesting findings are revealed. At 135 °C, the viscosity values for the 20L, 20L1S, and 20L3S samples are 570, 495, and 407 mPa·s, respectively. Adding 1 % Sasobit to the 5, 10, and 20 % lignin-modified samples resulted in an 11 % decrease in viscosity. Furthermore, the addition of 3 % Sasobit in all lignin-modified bitumen demonstrates a more substantial viscosity reduction, reaching approximately 22 %. These results indicate Sasobit's potential to neutralise the viscosity-raising effect of Kraft lignin. In a combined system, the dispersing and disruptive capabilities of Sasobit may mitigate the viscosity-enhancing effects of Kraft lignin. Sasobit potentially reduces the complex molecular interactions caused by the Kraft lignin, leading to a moderated and optimised viscosity in the lignin-modified bitumen. It's crucial to note that the mixing process directly contributes to a 9 % viscosity increase. This suggests that in a dry process, the efficacy of Sasobit in reducing the viscosity of lignin-modified bitumen might be even more significant than what's observed in these results. As depicted in Figure 6.12, the viscosity of the VB is notably comparable to that of the 5L3S sample. The viscosity of the VB and 5L3S samples are 303 and 291 mPa·s at 135 °C, respectively. However, it's essential to consider the influence of the mixing process on these results.

After the detailed evaluation of viscosity variations of bitumen samples, another crucial aspect is the mixing and compaction temperatures of asphalt mixes. Understanding these temperatures is fundamental as they play a crucial role in ensuring that the asphalt mix maintains its optimum workability and performance during production and compaction. BRV is used to measure the viscosity of bitumen, typically at a temperature of 135 °C, to ensure that bitumen can be easily pumped at the asphalt plant. Moreover, a corresponding viscosity value taken at 165 °C facilitates the establishment of a viscosity-temperature relationship. This relationship is useful in determining the optimal mixing and compacting temperatures for asphalt mixes. As a general guideline, the bitumen used in preparing the asphalt mixes must be heated to the range of mixing and compaction temperatures to produce a viscosity of 170 ± 20 and 280 ± 30 mPa·s respectively (ASTM D6926 standard). These parameters, obtained from empirical studies, indicate the importance of maintaining appropriate viscosities during asphalt production and compaction.

Figure 6.13 illustrates the linear relationship, in a semi-logarithmic scale, between viscosity and temperature for VB, 3S, 5L3S, 10L3S, and 20L3S samples at tested temperatures. Based on this diagram, it is possible to estimate accurately the desired temperatures for mixing and compaction of the asphalt mixes. According to Figure 6.13, the mixing and compaction temperatures of the asphalt mixes containing the VB sample are 148 and 137 °C, respectively. VB values are used as the reference point for subsequent sample comparisons. Adding Sasobit leads to a decrease in these temperatures, reaching 144 and 133 °C respectively, underlining Sasobit's efficacy and potential environmental benefits. In contrast, the addition of Kraft lignin increases viscosity, resulting in increased mixing and compaction temperatures. For lignin-modified samples containing 3 % Sasobit, the mixing temperatures are 147, 150, and 157 °C for the 5L3S, 10L3S, and 20L3S samples, respectively. This trend is also observed in the compaction temperatures of the corresponding samples. Although a general upward trend in temperature is observed with increased Kraft lignin content, the presence of Sasobit causes a downward shift in both mixing and compaction temperatures when compared to lignin-modified bitumen samples without Sasobit. This data reveals the synergistic effect of Sasobit and Kraft lignin. As a result, Sasobit emerges as an effective solution to counterbalance the increased mixing and compaction temperatures associated with lignin-modified bitumen.

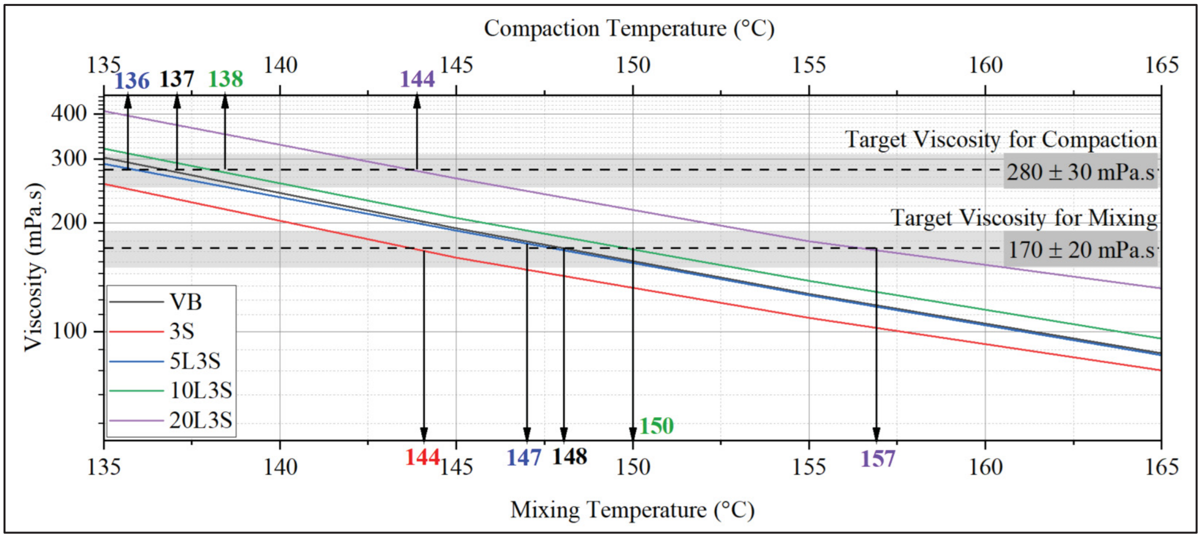


Figure 6.13 Average target viscosities for mixing and compaction and average corresponding temperatures for VB, 3S, 5L3S, 10L3S, and 20L3S samples

Table 6.3 Average mixing and compaction temperature (T_{mixing} and $T_{compaction}$) and corresponding temperature changes (ΔT_{mixing} and $\Delta T_{compaction}$) compared to VB bitumen for all bitumen samples

Parameter \ Sample	T_{mixing} (°C)	$\Delta T_{mixing\ compared\ to\ VB}$ (°C)	$T_{compaction}$ (°C)	$\Delta T_{compaction\ compared\ to\ VB}$ (°C)
VB	148	0	137	0
VBM	150	+2	138	+1
1S	147	−1	136	−1
3S	144	−4	133	−4
5L	152	+4	141	+
5L1S	150	+2	138	+1
5L3S	147	−1	136	−1
10L	155	+7	144	+7
10L1S	152	+4	140	+3
10L3S	150	+2	138	+1
20L	165	+17	151	+14
20L1S	161	+13	148	+11
20L3S	157	+9	144	+7

The addition of 3 % Sasobit leads to a reduction in the mixing and compaction temperatures by 4 °C. These temperature reductions, however, are less than those typically achieved in the production of warm mix asphalt (WMA) with Sasobit, reflecting the variability in its effectiveness depending on whether the process is wet or dry. Hence, Sasobit's effectiveness is more significant in asphalt mixes than in bitumen. Generally, the addition of 3 % Sasobit can reduce the mixing and compaction temperatures of WMA by approximately 30 °C, from 150 to 120 °C (ΔT_{mixing}) and from 135 to 105 °C ($\Delta T_{compaction}$), respectively (SasolChemicals, 2025). In contrast, the addition of 20 % Kraft lignin has the opposite effect, increasing the mixing and compaction temperatures by 17 and 14 °C, respectively (T_{mixing} compared to VB = + 17 and $\Delta T_{compaction}$ compared to VB = + 14), which are fairly high values, comparable to those required for polymer bitumens (red values) (Table 6.3). These findings are in accordance with those reported in laboratory research by Al-falahat et al. on two unmodified bitumens (PG 52S−34 and PG 58S−28) with the same lignin contents (Al-falahat et al., 2024).

6.6.4 DSR results

Figure 6.14 and 6.15 illustrate the test results of DSR on bitumen samples at high temperatures. These results provide insights into the sample's rheological properties, which play a significant role in determining the performance of the flexible pavement surface materials. These properties specifically include the potential rutting performance, stiffness, and viscoelastic behavior. Rutting, or permanent deformation, is a major distress mode in asphalt pavements. The rutting parameter derived from the DSR test is the high-temperature |G*|/sin(δ) where a greater value of |G*|/sin(δ) indicates a better potential for rutting resistance (Domingos & Faxina, 2016). There is a correlation between the two parts of the rutting parameter since a higher |G*| represents a stiffer binder, while a lower δ denotes increased elasticity. Combining these two parameters suggests a bitumen characterised by both stiffness and elasticity, establishing an ideal behavior for resisting rutting at high temperatures.

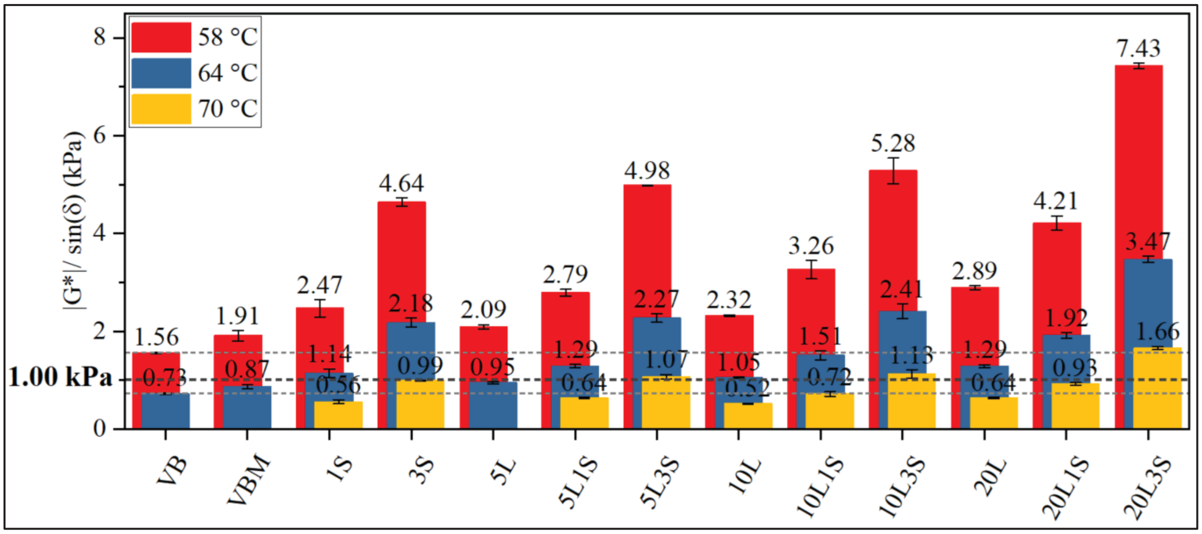


Figure 6.14 Effect of Kraft lignin, Sasobit, and their combination on the |G*|/sin(δ) of bitumen at 58, 64, and 70 °C (error bars based on two replicates)

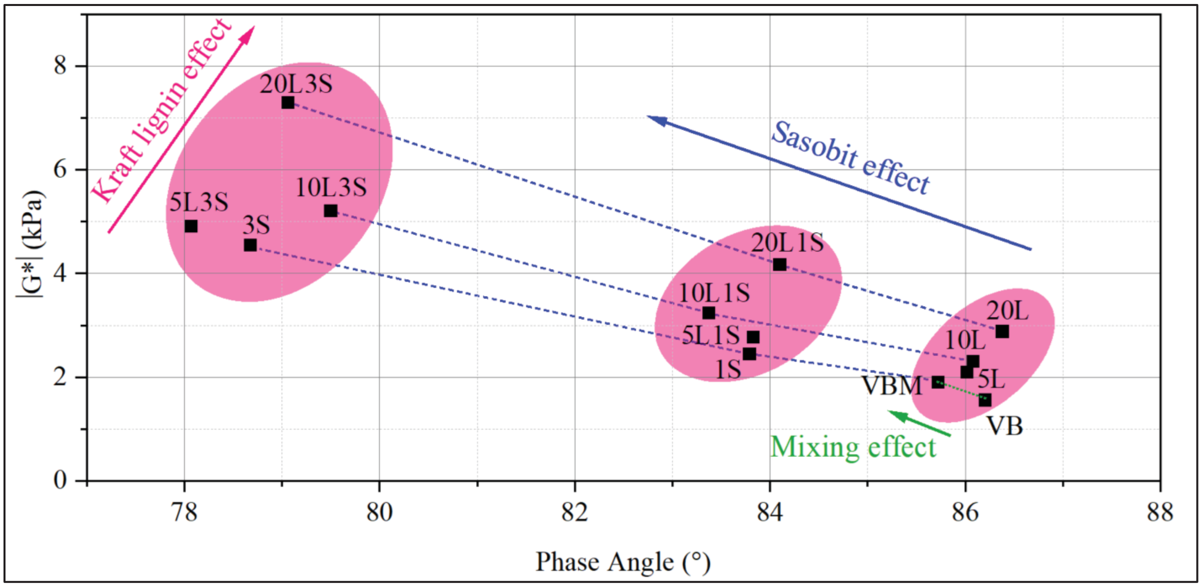


Figure 6.15 Norm of complex shear modulus ($|G^*|$) and phase angle (δ) of samples at 58 °C using DSR test

Figure 6.14 shows |G*|/sin(δ) values for all bitumen samples at temperatures of 58, 64, and 70 °C. All samples pass the minimum required |G*|/sin(δ) value of 1.00 kPa for unaged asphalt binders in accordance with Performance Grade (PG) specifications (4101 standard of MTMD), but at different temperatures. Compared to the virgin bitumen (VB) sample, all modified samples show higher |G*|/sin(δ) values. By adding Sasobit to bitumen, |G*|/sin(δ) values at 58 and 64 °C improve by 57 % and 198 % on average for 1S and 3S samples, respectively. Kraft lignin's inclusion in the 5L, 10L, and 20L samples enhances the |G*|/sin(δ) values by averages of 32, 46, and 81 % respectively at the same temperatures. From a synergistic perspective, adding 1 % Sasobit to lignin-modified bitumen samples (5, 10, and 20 %) enhances the |G*|/sin(δ) values nearly equivalent to the addition of 1 % Sasobit to the VB, with an approximate increase of 50 %. However, when 3 % Sasobit is introduced, the |G*|/sin(δ) values for the lignin-modified bitumen with 10 and 20 % Kraft lignin show almost the same increase as the VB sample. Through the addition of 20 % Kraft lignin and 3 % Sasobit to bitumen (20L3S), |G*|/sin(δ) value improves by 376 % compared to VB.

The norm of the complex shear modulus (|G*|) quantifies the stiffness of bitumen, while the phase angle (δ) indicates its viscoelastic behavior. The rheological properties of bitumen include both elastic and viscous deformations. Ideally, a bitumen should have a balance between these elastic and viscous properties to effectively resist diverse (mechanical and thermal) pavement stresses (Airey, Rahimzadeh, & Collop, 2002).

Figure 6.15 shows the norm of complex shear modulus (|G*|) and phase angle (δ) of all bitumen samples at 58 °C. As shown in Figure 6.15, the mixing process slightly affects the stiffness and viscoelastic properties of the VBM sample in comparison to the VB sample. While the mixing process causes a slight increase in the bitumen's stiffness (|G*|), it has an almost negligible effect on the δ value.

Sasobit has a significant effect on the bitumen's rheological properties. |G*| values for VB, 1S, and 3S samples are 1.56, 2.45, and 4.55 kPa, respectively (Figure 6.15). This implies an enhancement in stiffness with the addition of Sasobit. In terms of δ value, VB, 1S, and 3S samples measure 86.2, 83.8, and 78.7 °, respectively, indicating that the addition of Sasobit to bitumen increases its elasticity and reduces its viscous behavior.

The addition of Kraft lignin to bitumen also influences its rheological properties. The |G*| values for the VB, 5L, 10L, and 20L samples are 1.56, 2.09, 2.31, and 2.88 kPa, respectively, indicating an upward trend in stiffness with increasing Kraft lignin content (Figure 6.15). As the Kraft lignin content increases in these samples, there's a corresponding increase in |G*| values. As observed in the BRV results, the addition of Kraft lignin increases the viscosity of modified bitumen (see previous section: 6.6.3). Since the higher the viscosity of bitumen, the higher its complex shear modulus, the results of these two tests confirm each other. However, it's noteworthy to highlight that the stiffness of the 20L sample is still lower than that of the 3S sample. Based on the δ values, VB, 5L, 10L, and 20L samples are 86.2, 86.0, 86.1, and 86.4 °, respectively. While the viscoelastic behaviors of the 5L and 10L samples remain relatively consistent, the 20L sample shows a slight increase in viscosity. These results demonstrate slight variations of δ due to varying Kraft lignin concentrations.

The synergistic effect of Sasobit and Kraft lignin as bitumen additives on the rheological properties of bitumen is significant. Considering the lignin-modified bitumen with 20 % Kraft lignin, the |G*| value for 20L, 20L1S, and 20L3S samples are 2.88, 4.18, and 7.29 kPa, respectively (Figure 6.15). These results suggest that the addition of Sasobit to lignin-modified bitumen increases its stiffness at 58 °C. Additionally, δ values for 20L, 20L1S, and 20L3S are 86.4, 84.1, and 79.1 °, respectively, indicating that Sasobit enhances the elasticity of lignin-modified bitumen. A similar trend is observed for bitumens modified with 5 and 10 % Kraft lignin but at a reduced intensity. Generally, higher Sasobit content correlates with increased stiffness and elasticity. These findings are promising, as Sasobit has the potential to enhance the rheological properties of lignin-modified bitumen in the intended direction.

The high temperature (T_{high}) values determined according to ASTM D 7643 standard for VB, 20L, 3S, and 20L3S samples are shown in Table 6.4 (reference sample and samples containing the most additives). These results illustrate the significant impact of Sasobit and Kraft lignin on the high-temperature performance of bitumen. The inclusion of Sasobit and Kraft lignin in bitumen increases the Thigh values. This increment demonstrates that Sasobit effectively raises the high-temperature performance threshold of lignin-modified bitumen, making the bitumen better at high temperatures.

Table 6.4 Values of $|G^*|/\sin(\delta)$, and corresponding high temperature (T_{high}) and high temperature grade (H-grade) for VB, 20L, 3S and 20L3S samples

Sample	$|G^*|/\sin(\delta)$ (kPa)			T_{high}	H-grade^{A}
(code)	at 58 °C	at 64 °C	at 70 °C	(°C)	(°C)
VB	1.56	0.73	---	$61.5 \geq 58$	58
20L	2.89	1.29	0.64	$65.9 \geq 64$	64
3S	4.64	2.18	0.99	$70.2 \geq 64$	64
20L3S	7.43	3.47	1.66	$73.8^{B} \geq 70$	70

^{A} Increment of 6 °C.

^{B} T_{high} value determined despite missing value of $|G^*|/\sin(\delta)$ under 1.00 kPa.

6.6.5 MSCR results

The MSCR test results provide valuable insight into the enhanced performance characteristics of modified bitumen, as demonstrated through their impact on non-recoverable creep compliance values. Figure 6.16 and Figure 6.17 show the MSCR test results for VB, 20L, 3S, and 20L3S samples at 52, 58, and 64 °C, i.e. at high temperatures. The non-recoverable creep compliance at 0.1 and 3.2 kPa ($J_{nr0.1}$, $J_{nr3.2}$), and the difference in non-recoverable creep compliance between the two stress levels (J_{nrdiff}) are key indicators of the bitumen's behavior under different levels of stress.

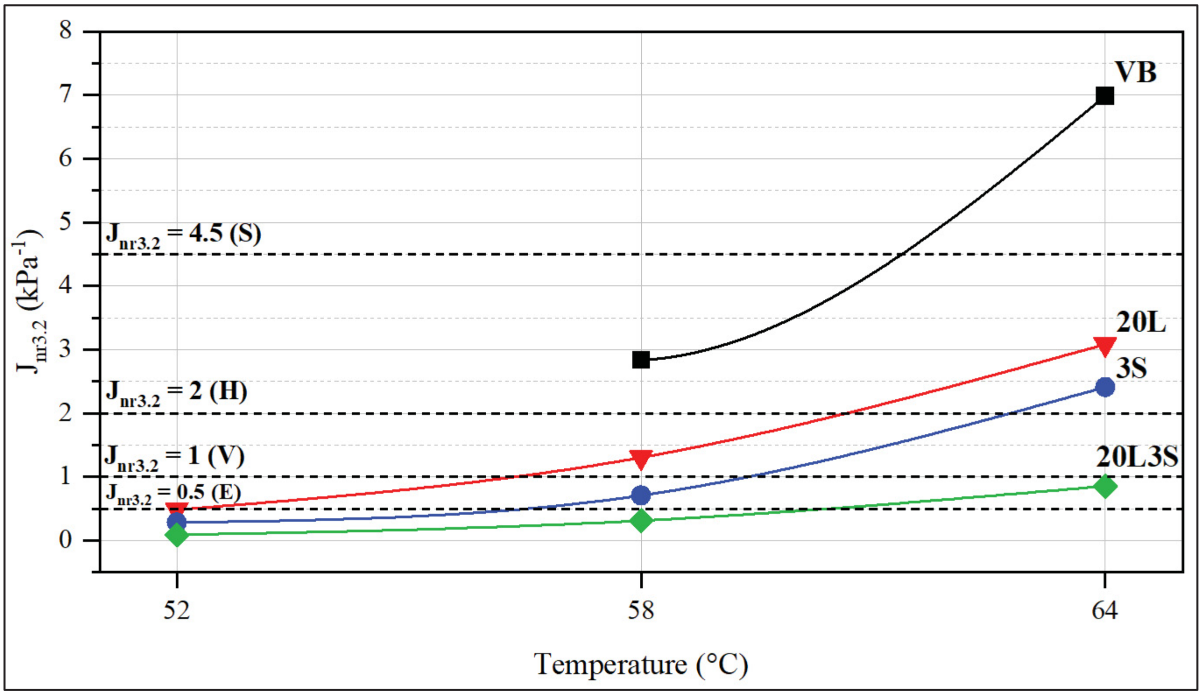
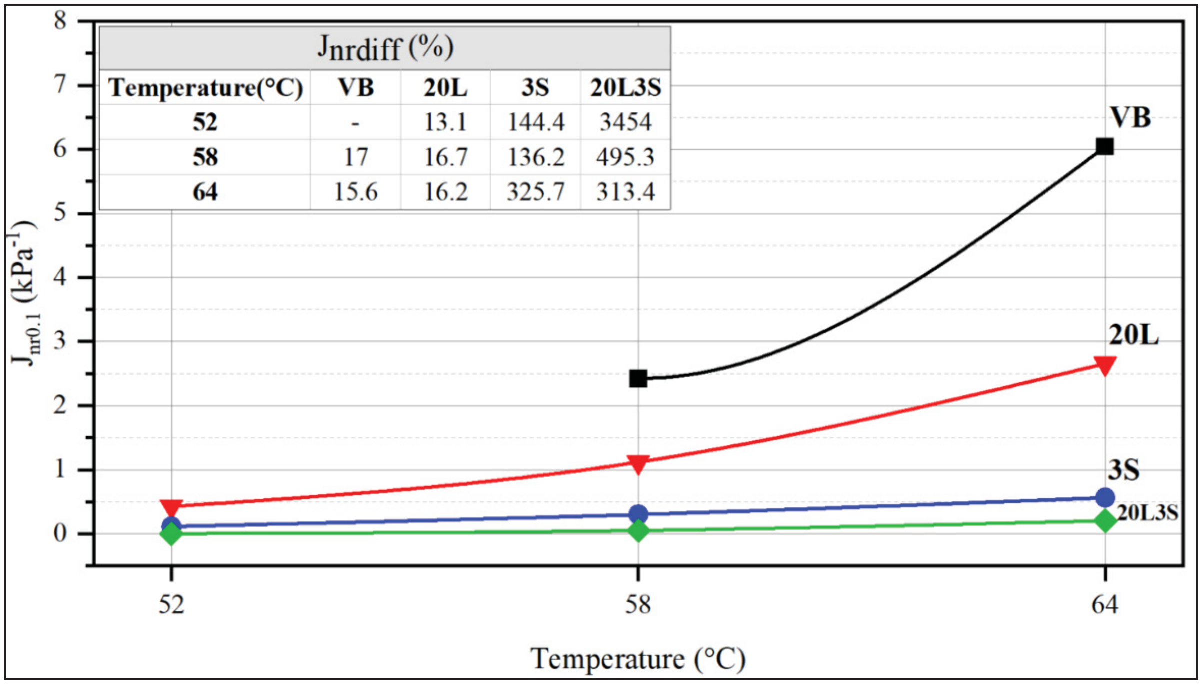


Figure 6.16 Non-recoverable creep compliance at 3.2 kPa ($J_{nr3.2}$) of VB, 20L, 3S, and 20L3S samples as a function of temperature (52, 58, and 64 °C) (traffic level class indicated in brackets: S for standard, H for high, V for very high, and E for extreme)



Jnrdiff (%)

Temperature(°C)	VB	20L	3S	20L3S
52	-	13.1	144.4	3454
58	17	16.7	136.2	495.3
64	15.6	16.2	325.7	313.4

Figure 6.17 Non-recoverable creep compliance at 0.1 kPa ($J_{nr0.1}$) and the difference in non-recoverable creep compliance (J_{nrdiff}) of VB, 20L, 3S, and 20L3S samples at 52, 58, and 64 °C

As illustrated in Figure 6.16, the addition of Kraft lignin to the bitumen results in a decrease in $J_{nr3.2}$ values across all temperatures, which is associated with an increased resistance to permanent deformation. This behavior is indicative of an enhanced rutting resistance. Incorporating 3 % Sasobit into bitumen, similar to the 20L, reduces $J_{nr3.2}$ thereby improving rutting resistance. Notably, the 3S sample demonstrates an even lower $J_{nr3.2}$ value than the 20L sample. For the 20L3S sample, the co-incorporation of Sasobit and Kraft lignin results in the lowest $J_{nr3.2}$ value. This suggests a significant increase in the material's elasticity, corresponding to a reduced unrecovered strain and pointing towards improved rutting resistance.

As Figure 6.17 illustrates, this trend is also observed in the $J_{nr0.1}$ results. The difference between non-recoverable creep compliance (J_{nrdiff}) provides insights into how the bitumen sample behaves under different levels of stress. $J_{nr0.1}$ is measured under a lower stress level and $J_{nr3.2}$ under a higher stress level. The difference between these values is expressed as a percentage.

An increase in J_{nrdiff} indicates a higher sensitivity of the bitumen to changes in applied stress. In practical terms, it shows that the binder behaves differently under higher stresses than it does under lower stresses. As shown in the table in Figure 6.17, the J_{nrdiff} for both VB and 20L samples show little deviation across temperatures, implying consistent performance across stress levels. However, for the 3S and 20L3S samples, the relatively minor values for $J_{nr0.1}$ and $J_{nr3.2}$ at 52, 58, and 64 °C and a small difference between those values result in a significant percentage increase for J_{nrdiff}. In this context, these heightened J_{nrdiff} percentages make this parameter less meaningful for 3S and 20L3S samples at the tested temperatures due to the relatively low J_{nr} values. The MSCR test results demonstrate the potential of Sasobit and Kraft lignin, both separately and synergistically, to enhance the performance of bitumen at high temperatures.

Table 6.5 shows the MSCR parameters including the non-recoverable creep compliance ($J_{nr3.2}$), the difference in non-recoverable creep compliance between 0.1 and 3.2 kPa (J_{nrdiff}), average recovery of strain ($R_{3.2}$) at 58 °C, and traffic level (n) values for VB, 20L, 3S, and 20L3S samples. According to the $J_{nr3.2}$ value, the VB, 20L, 3S, and 20L3S samples have standard (S), heavy traffic (H), very heavy traffic (V), and extremely heavy traffic (E) resistance to traffic, respectively. However, when considering all test parameters, specifically, the very low values for $R_{3.2}$, all samples exhibit a standard (S) level of traffic resistance.

Table 6.5 Requirements and traffic level (n) class of VB, 20L, 3S, and 20L3S samples obtained from MCSR test results at 58 °C

Sample (code)	$J_{nr3.2}$ (kPa^{-1})	J_{nrdiff} (%)	$R_{3.2}$ (%)^{A}	$n_{obtained}$ (letter)
VB	$2.83 \leq 4.5$ (S)	$17.0 \leq 75$ (ok)	0.85 (S)	S
20L^{B}	$1.31 \leq 2$ (H)	$16.7 \leq 75$ (ok)	$1.5 \geq 27.4$ (no)	S
3S^{B}	$0.71 \leq 1$ (V)	$136.2 \leq 75$ (no)	$11.6 \geq 32.1$ (no)	S
20L3S^{B}	$0.31 \leq 0.5$ (E)	$495.3 \leq 75$ (no)	$16.3 \geq 40.0$ (no)	S

^{A}Requirement: $R_{3,2} \geq 29{,}371\ J_{nr3,2}{}^{-0{,}263}$, but does not apply to bitumen with a traffic level class S.

^{B}For samples 20L, 3S and 20L3S, MCSR values at 64, 64 and 70 °C (corresponding to the H-grade: Table 6.4) respectively could have been taken into account in determining the traffic level class, but this would not have altered the n values obtained.

6.6.6 BBR results

The BBR test results are crucial in evaluating the low-temperature behavior of bitumen, providing insights into the material's flexibility and resistance to thermal cracking. Figure 6.18 and Table 6.6 present the BBR test results for VB, 20L, 3S, and 20L3S samples.

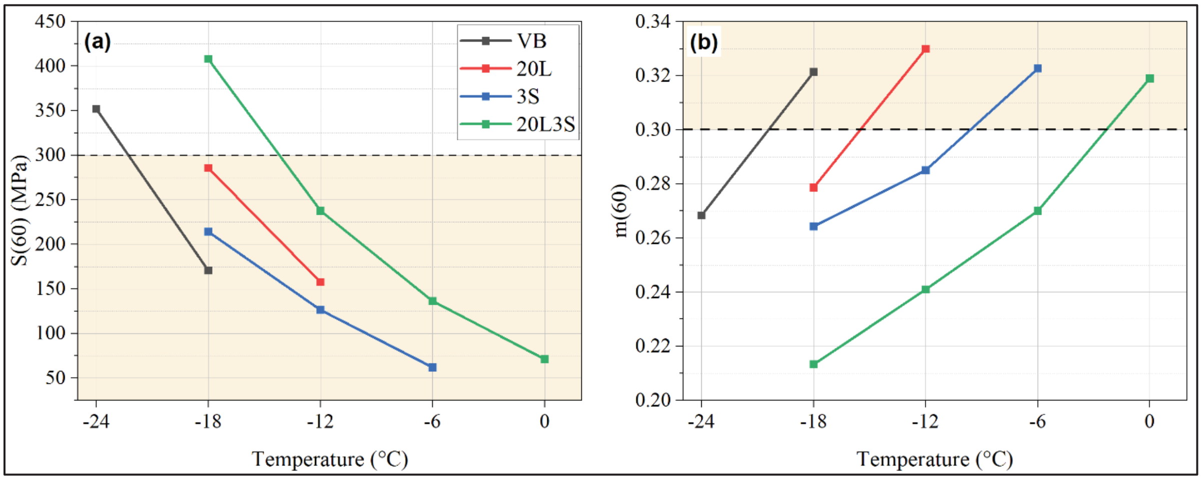


Figure 6.18 Effect of Sasobit and Kraft lignin on (a) creep stiffness modulus S(60) and, (b) creep relaxation m(60) for VB, 20L, 3S, and 20L3S samples at different low temperatures using the BBR test (yellow areas: suitable values)

Table 6.6 BBR test results and corresponding low temperature (T_{low}) and low temperature grade (L-grade) of bitumen for VB, 20L, 3S, and 20L3S samples

Sample (code)	T_T (°C)[A]	S(60) (MPa)	m(60)	T_{low} (°C)[B]	L-grade[C] (°C)
VB	−24	352	0.268	−30.4 ≤ −28	−28
	−18	171	0.321		
20L	−18	286	0.279	−25.5 ≤ −22	−22
	−12	158	0.330		
3S	−18	214	0.264	−19.6 ≤ −16	−16
	−12	127	0.285		
	−6	62	0.323		
20L3S	−18	408	0.213	−12.3 ≤ −10	−10
	−12	238	0.241		
	−6	137	0.270		
	0	71	0.319		

[A] T_T: testing temperature. Through correlations, it was determined that it was possible to test the bitumen at a temperature 10 °C above the target temperature as specified in the standard.

[B] T_{low} is calculated from the most restrictive of those parameters: S(60) value lower than 300 MPa and m(60) value higher than 0.3.

[C] Increment of 6 °C.

Figure 6.18a and b show the effect of Sasobit and Kraft lignin on the creep stiffness modulus S(60) and creep relaxation m(60), respectively, for VB, 20L, 3S, and 20L3S samples at different low temperatures. These parameters are crucial indicators of the bitumen's low-temperature performance.

To determine the low-temperature performance of bitumen, two key criteria must be met: S(60) < 300 MPa and m(60) > 0.3, as per AASHTO M320. The highlighted areas (yellow zone) in Figure 6.18 show recommended values to determine the lower grade of bitumen. For VB, the testing began at −24 °C, where both S(60) and m(60) did not meet the criteria. The temperature was then increased to −18 °C (according to AASHTO M320 the temperature increment is 6 °C), where the sample passed the performance thresholds. For the modified binders (3S, 20L, and 20L3S), the initial testing started at −18 °C. For 20L, the S(60) criterion was met, but m(60) did not pass, so the temperature was increased to −12 °C, at which point both criteria were satisfied. Similarly, for 3S, while S(60) passed at −18 °C, m(60) did not. Testing was continued at −12 and −6 °C, where the m(60) criterion was eventually met at −6 °C. For 20L3S, the testing temperature was increased up to 0 °C to achieve conformity with both S(60) and m(60). While it would have been possible to test all samples at the same temperatures, the low-temperature determination method was selected to identify the specific threshold at which each sample meets the performance criteria.

Incorporating 20 % Kraft lignin into bitumen, as shown in Figure 6.18a, increases the S(60) while reducing the m(60) values (Figure 6.18b). This indicates that the 20L sample becomes stiffer and exhibits a reduced ability to relax thermal stresses, implying reduced flexibility, which could heighten the risk of thermal cracking. For the 3S sample, the test results reveal a slight increase in S(60) but not to the extent observed in the 20L sample, while the m(60) value is even lower than that of 20L and significantly lower than VB. These findings suggest that the addition of 3 % Sasobit reduces low-temperature performance. The 20L3S sample exhibits the highest increase in creep stiffness and the lowest m(60) relaxation parameter. This indicates that the synergistic effect of Sasobit and Kraft lignin intensifies the S-value and the m-value decreases. Consequently, these test results suggest that adding 20 % Kraft lignin and 3 % Sasobit may adversely affect the bitumen's low-temperature performance.

Table 6.6 shows the BBR test outcomes and calculated T_{low} based on S(60) and m(60) according to ASTM D 7643 standard. Test results show a shift in the low-temperature grading (L-grade), moving from −28 °C for VB to −22 °C, −16 °C, and −10 °C for the 20L, 3S, and 20L3S samples, respectively. This shift to higher temperature signifies a notable alteration in the bitumen's lower grade. These findings demonstrate that modifying bitumen with Sasobit and Kraft lignin, particularly in combination, significantly decreases low-temperature performance. It remains to be seen whether this performance will be as critical for warm mix asphalt (WMA).

6.6.7 Integrated analysis between tests, and rheological and chemo-thermal properties

To gain an overview of the results and understand the multifaceted impacts of additives, this section focuses on an integrated analysis that investigates their general effects across tests focused on rheological and chemo-thermal properties, highlighting how these interactions contribute to the overall performance of bitumen.

Kraft lignin significantly alters the properties of bitumen, increasing viscosity, at very high temperatures (135–165 °C), and enhancing stiffness at both high and low temperatures. While it improves high-temperature performance, it also makes the bitumen more brittle at low temperatures, increasing its susceptibility to cracking. Notably, these changes occur without any signs of chemical interaction as observed through FTIR analysis. Thermal analysis reveals that Kraft lignin's complex biochemical composition contributes to higher mass loss at lower temperatures due to the degradation of some of its components. Conversely, at very high temperatures, certain elements of Kraft lignin enhance the thermal stability of bitumen by acting as barriers against thermal degradation.

Sasobit uniquely modifies the properties of bitumen. By decreasing the viscosity at very high temperatures (135–165 °C), Sasobit enhances the high-temperature performance of bitumen, increasing its resistance to rutting by increasing both shear modulus and elasticity. However, Sasobit's influence at low temperatures presents challenges. Sasobit’s crystalline structure leads to reduced flexibility because of increased brittleness, resulting in a shift in its low-temperature grading. Physical interaction between Sasobit and bitumen and specific properties such as melting point and chemical structure of Sasobit are primary reasons for modifying its rheological properties, enhancing stiffness, and reducing viscosity and stability within the operational temperature range (< 200 °C), but at very high temperatures.

In the combined system, the properties of both Sasobit and Kraft lignin are effectively utilised, producing a synergistic effect. The increased viscosity, at very high temperatures (135–

165 °C), typically seen with lignin-modified bitumen is moderated by the addition of Sasobit, enhancing the mixture's workability and optimising compaction and mixing temperatures. Additionally, the high-temperature performance is enhanced, leading to increased rutting resistance. The 20L3S sample exhibits the highest shear modulus and elasticity, as demonstrated by the MSCR test results. However, a significant drawback is the excessive stiffness at low temperatures, which adversely affects the low-temperature performance. No chemical reactions are observed when Sasobit and Kraft lignin are combined with bitumen, indicating that their impacts are mainly physical and similar to their individual effects. From a thermal sensitivity perspective for the modified bitumen, and according to the presented results, the influence of Kraft lignin is more significant than that of Sasobit to alter the behavior of the combined system.

6.7 Conclusion

In this laboratory study, the separate and synergistic effects of Sasobit at concentrations of 0, 1, and 3 % and Kraft lignin at concentrations of 0, 5, 10, and 20 % on the rheological and chemo-thermal properties of bitumen, were investigated. A series of tests and analyses were conducted to evaluate the effect of these additives, which included the Fourier-transform infrared spectroscopy (FTIR) technique, thermogravimetric analysis (TGA), and Brookfield rotational viscometer (BRV), dynamic shear rheometer (DSR), multiple stress creep recovery (MSCR) and bending beam rheometer (BBR) tests. These tests and analyses have provided valuable insights into the interactions between Sasobit, Kraft lignin, and bitumen. The findings from the conducted tests are summarised as follows:

- FTIR spectra confirm that the incorporation of both Kraft lignin and Sasobit into the bitumen does not result in chemical reactions which can be attributed to the physical distribution and interactions rather than any chemical modifications.
- TGA highlight the influence of additive type and content on thermal stability. Higher Kraft lignin content leads to reduced thermal stability, meanwhile, low Sasobit

concentrations slightly improve thermal stability, but higher concentrations do not enhance it.

- In terms of the operational temperature of the asphalt mix (< 200 °C), Kraft lignin's inclusion leads to a higher degradation rate in lignin-modified bitumen as observed with the TGA results. The addition of Sasobit shows a negligible effect on this temperature range of bitumen.
- Sasobit and Kraft lignin have counteractive effects on bitumen viscosity. While Kraft lignin increases viscosity, Sasobit is effective in reducing it. Sasobit has the potential to optimise lignin-modified bitumen viscosity to desired levels. The optimal combination to achieve similar viscosity levels as VB is found in the 5L3S sample (5 % Kraft lignin and 3 % Sasobit).
- Kraft lignin causes increased mixing and compaction temperatures of asphalt mix meanwhile, Sasobit decreases these temperatures. In the 5L3S sample (5 % Kraft lignin and 3 % Sasobit), these effects offset each other, resulting in mixing and compaction temperatures of 147 and 136 °C, respectively, which are similar to those of virgin bitumen (148 and 137 °C).
- Based on DSR results, the modifications with Sasobit and Kraft lignin both individually and in combination show an increase in the $|G^*|/\sin(\delta)$, the potential rutting resistance, of modified bitumen. In terms of viscoelastic behavior, Sasobit enhances both the shear modulus (increasing $|G^*|$) and elasticity (reduction of the phase angle, δ) of bitumen. Kraft lignin increases the shear modulus of bitumen with negligible effect on elasticity. The inclusion of Sasobit and Kraft lignin in bitumen increases its high temperature (T_{high}) and high temperature grade (H-grade).
- MSCR test results show that the co-incorporation of Sasobit and Kraft lignin results in a significant decrease in non-recoverable creep compliance ($J_{nr3.2}$) and an increase in average recovery of strain ($R_{3.2}$), but insufficient to improve the traffic resistance (the n class).
- Finally, Sasobit and Kraft lignin significantly increase stiffness and brittleness at low temperatures and reduce the bitumen’s low-temperature performance (T_{low} and L-grade).

The outcomes of this study offer a clear and comprehensive understanding of how Kraft lignin and Sasobit can be utilised to modify the properties of bitumen, focusing on chemo-thermal and rheological properties. The findings demonstrate the potential of Sasobit to counterbalance some of the challenges posed by Kraft lignin and the adverse effects associated with lignin-modified bitumen, particularly in terms of viscosity. Moreover, these two additives increase the mechanical performance of bitumen at high temperatures but reduce its performance at low temperatures. The insights gained from this research are expected to significantly influence future developments in asphalt mixture design, leading the industry towards more environmentally sustainable and energy-efficient practices.

6.8 Further developments

Further investigations are required to fully understand the other aspects of using Sasobit and Kraft lignin in bitumen modifications. This includes life cycle assessment (LCA) for quantifying the environmental impact, long-term performance effects by conducting trial sections in real traffic and weather conditions, and the economic feasibility of these modifications on bitumens in real-world applications.

This study is part of an ongoing project to investigate the feasibility and performance of using Kraft lignin as an additive or partial replacer of modified and unmodified bitumens, and cold, warm, and hot mix asphalts, and future publications will cover these aspects. The next phase of our ongoing project will focus on a laboratory study of the application of warm mix asphalt (WMA) incorporating Kraft lignin and Sasobit, aiming to further understand and enhance the sustainable use of this material in asphalt mixtures.

CHAPTER 7

LABORATORY STUDY ON THE EFFECT OF KRAFT LIGNIN AND SASOBIT® ON CONSTRUCTION TEMPERATURES, COMPACTABILITY AND PHYSICAL PROPERTIES OF HOT AND WARM MIX ASPHALT

Ali Rezazad Gohari[a], Sébastien Lamothe[a], Jean-Pascal Bilodeau[b], Ahmad Mansourian[c] and Alan Carter[a]

[a] Département de Génie de La Construction, École de Technologie Supérieure (ÉTS), 1100 Notre-Dame Ouest, Montréal, QC, Canada, H3C 1K3.
[b] Département de Génie Civil et de Génie Des Eaux, Université Laval, 1065 avenue de la Médecine, Québec, QC, Canada, G1V 0A6.
[c] Bitumen and Asphalt Department, Road, Housing and Urban Development Research Center, Marvi St., Farhangian St., Sheikh Fazlollah Highway, Tehran, Iran, P9Q8+99J.

Paper Submitted in *Journal of Construction and Building Materials*, December 2024

7.1 Abstract

This study investigates the feasibility of using Kraft lignin, a sustainable and renewable biopolymer, in Hot and Warm Mix Asphalt (HMA and WMA), with a particular focus on its integration alongside Sasobit®, a WMA additive. The research aims to evaluate the impact of Kraft lignin and Sasobit, individually and in combination, on the construction temperatures, compactability, and physical properties of asphalt mixtures. The experimental program included a reference HMA and modified mixes with 20 % Kraft lignin, 3 % Sasobit, and their combination. These mixes were designed and subjected to tests to assess their volumetric and mass properties and to determine the construction temperatures using the Superpave Gyratory Compactor (SGC) tests at different construction temperatures. The results demonstrated that adding Kraft lignin increased construction temperatures due to its impact on binder viscosity, while Sasobit effectively reduced these temperatures by lowering binder viscosity. When used together, Sasobit offset the increase in construction temperatures caused by Kraft lignin, resulting in compaction temperatures similar to the reference HMA mix. Additionally, Kraft lignin increased air voids leading to reduced compactability, at higher gyration levels. It also exhibited a dual role, functioning as both a binder replacement and a filler. In conclusion, the combination of 20 % Kraft lignin with 3 % Sasobit offers a promising solution for enhancing the sustainability of asphalt mixtures.

Keywords: Kraft lignin, Sasobit®, Hot Mix Asphalt, Warm Mix Asphalt, Volumetric properties, Construction temperatures.

7.2 Introduction

Roads and highway networks have significantly enhanced global connectivity, making the world more interconnected than ever. In recent decades, the growing traffic volumes have made highway expansion and the rehabilitation of existing roads and streets imperative (Diene, 2024). Asphalt pavements are preferred for their cost-effectiveness, smooth surface, and efficient load distribution characteristics (F. Wang et al., 2021). Despite these benefits, asphalt pavement contributes significantly to the ecological challenges of road construction due to its air pollution, energy consumption, and reliance on natural resources. Growing awareness of these impacts has shifted the focus in the asphalt industry toward sustainable development (Balaguera, Carvajal, Albertí, & Fullana-i-Palmer, 2018). Sustainability involves balancing economic, social, and environmental considerations to promote long-term development (Munasinghe, 1993). For asphalt mixes, sustainable practices aim to reduce greenhouse gas (GHG) emissions, lower resource consumption, reduce the dependency on natural resources, and enhance pavement durability through the application of advanced techniques and additives (Mansourian et al., 2019; Pouranian & Shishehbor, 2019).

In light of increasing global environmental concerns, advancements in technologies aimed at reducing the environmental footprint of asphalt pavements have gained momentum. Two key approaches to enhancing sustainability involve the implementation of energy-efficient production methods and the incorporation of additives that help reduce the environmental footprint (Hegab et al., 2023). One of the most effective strategies for advancing sustainability in asphalt production is through innovations in the asphalt mix's construction temperatures, which have a direct and significant impact on both energy consumption and emissions.

7.3 Background

7.3.1 Classification of Asphalt Mixtures by Construction Temperatures

Asphalt mixtures are classified by their construction temperatures into four main types: 1) Hot Mix Asphalt (HMA) is produced at temperatures ranging from 150-200 °C; 2) Warm Mix Asphalt (WMA) is produced at temperatures 10-45 °C lower than HMA; 3) Half Warm Mix Asphalt (HWMA) is produced at temperatures below 100 °C; and 4) Cold Mix Asphalt (CMA) is produced without heating the aggregates (Vaitkus, Čygas, Laurinavičius, Vorobjovas, & Perveneckas, 2016). HMA production is one of the major sources of GHG emissions, releasing substantial amounts of CO_2 (carbon dioxide), CH_4 (methane), and N_2O (nitrous oxide), and requiring high energy consumption due to the high construction temperatures (Hanson, Noland, & Cavale, 2012).

7.3.2 Warm Mix Asphalt (WMA)

WMA has emerged as a sustainable technology through substantial reductions in energy consumption and GHG emissions while enhancing working conditions by producing and placement of asphalt mix at lower mixing and compaction temperatures (Milad et al., 2022). This technology was initially developed in Europe in the 1990s and subsequently adopted in the United States in 2002 (Al-Rawashdeh, 2008). WMA has gained widespread adoption due to its significant environmental and economic benefits, making it a viable alternative to conventional HMA. Jamshidi et al. observed that lowering the production temperature by 10 °C results in a reduction of heavy oil consumption by 11.8 kWh and decreases CO_2 emissions by 1 kg per ton of asphalt. These energy savings also contribute to lower overall construction costs (Jamshidi, Hamzah, & You, 2013). Evaluations conducted in several European countries have shown that WMA technologies can significantly reduce harmful emissions during asphalt production (Capitão, Picado-Santos, & Martinho, 2012). T. Calabi-Floody et al. conducted a comparative study evaluating gas emissions and energy consumption between WMA, WMA-RAP, and HMA. The findings revealed that CO_2 emissions were reduced by up to 37 % in WMA-RAP, while energy consumption showed reductions ranging from 5 to 13 % (T. Calabi-Floody, A. Valdés-Vidal, Sanchez-Alonso, & A. Mardones-Parra, 2020).

WMA additives are generally categorized into organic additives, chemical additives, and foaming technologies. Organic additives, such as Sasobit®, reduce the viscosity of the binder at elevated temperatures. Chemical additives, such as Evotherm®, improve the adhesion between the binder and aggregates without altering the binder's viscosity. Foaming technologies include both additives and asphalt plant modifications. Additives such as Advera® and Asphamin®, introduce water into the binder, generating steam that temporarily expands the binder, thereby enhancing aggregate coating at reduced temperatures. Additionally, some foaming techniques involve directly injecting water into the asphalt mix during production, which requires plant modifications (Caputo et al., 2020). The proper selection and application of these additives are critical to optimizing the performance of WMA. Various types of WMA additives have been extensively evaluated from multiple perspectives, including their sustainability and environmental impacts, as well as their mechanical performance. Key factors such as rutting resistance, moisture susceptibility, fatigue, and thermal cracking have been thoroughly investigated across a wide range of studies. Several comprehensive review papers provide valuable insights into these aspects, providing in-depth analysis and critical evaluations (Abdullah et al., 2014; Behnood, 2020; Cheraghian et al., 2020; Diab, Sangiorgi, Ghabchi, Zaman, & Wahaballa, 2016; Guo et al., 2020; Jamshidi, Hamzah, & You, 2013; Prakash & Suman, 2022; Sukhija & Saboo, 2021).

7.3.3 Sasobit®

Among all WMA additives, Sasobit stands out as a key organic additive frequently applied in WMA technology and its impact on binder and asphalt mixture properties has been extensively studied. Sasobit melts at approximately 100 °C, aligning with the typical temperature range for WMA production. As the temperature drops, it forms a crystalline network within the binder, enhancing its stiffness, particularly at the in-service temperatures of the pavement (Edwards & Redelius, 2003). The main role of Sasobit is to reduce the viscosity of asphalt binder, resulting in lower construction temperatures (Ghuzlan & Al Assi, 2017). This reduction in viscosity directly contributes to the sustainability of asphalt mixtures. Based on literature and manufacturer guidelines, the recommended dosage of Sasobit should not exceed 4 % of the binder's weight, with 3 % being commonly recommended as the optimal amount (Edwards & Isacsson, 2005; Hainin et al., 2015; Jamshidi, Hamzah, & You, 2013).

Research on Sasobit can be categorized into two primary areas. The first area focuses on its use in WMA and its effects on the performance of asphalt mixtures. Sasobit has been shown to enhance rutting resistance by improving the high-temperature performance of the asphalt binder. At intermediate temperatures, it does not significantly affect the binder's resistance to fatigue cracking. However, at low temperatures, Sasobit can negatively impact binder performance, potentially reducing its resistance to cracking (Ghuzlan & Al Assi, 2017; C. Wang et al., 2013; Wasiuddin, Selvamohan, Zaman, & Guegan, 2007). The second area investigates Sasobit's function as a viscosity-reducing agent, and compaction aid, in various modified binders and asphalt mixtures, such as polymer-modified and rubber-modified binders (Akisetty, Gandhi, et al., 2010; Akisetty, Lee, et al., 2010; Edwards et al., 2010; Rossi et al., 2013). This property has been utilized in some studies recently (Gong et al., 2020; Tembe et al., 2023; D. Wu et al., 2023).

7.3.4 Lignin

The incorporation of bio-based additives, such as lignin, further enhances the sustainability of asphalt mixes by offering renewable alternatives or extenders to conventional petroleum-based binders. Kraft lignin, an organic byproduct of the paper industry, is derived from either softwood or hardwood (Kouisni et al., 2016). While current production costs are high due to limited industrial scale, lignin has the potential to become an economically feasible material as production scales up. As a renewable, non-toxic substance sourced from biomass (Feldman et al., 1986), lignin presents a promising solution for sustainable asphalt modification, particularly in countries such as Canada, where the vast availability of forest resources provides a significant green alternative. In recent years, significant attention has been focused on investigating the use of lignin in asphalt industry. Research studies consistently indicate that incorporating lignin into binder enhances performance at intermediate and high temperatures, though it can adversely affect low-temperature performance and cause challenges in compaction due to increased air voids. A major challenge with lignin as a binder additive is its tendency to increase viscosity, resulting in higher construction temperatures, which contradict sustainability objectives (Al-falahat et al., 2024; Arafat et al., 2019; Gao et al., 2020; Hobson, 2017; Lamothe, Al-falahat, Carret, & Carter, 2024; Lynam et al., 2018; Poeran, 2014; Ren et al., 2021; Sundstrom et al., 1983; J. Wu et al., 2021; Xie et al., 2017; C. Xu et al., 2021; G. Xu et al., 2017; Zahedi, Zarei, & Zarei, 2020; R. Zhang, Sun, et al., 2021; Y. Zhang, Wang, et al., 2020). In our previous studies (Rezazad Gohari et al., 2023; Rezazad Gohari, Lamothe, Bilodeau, Mansourian, & Carter, 2024), a significant increase in the viscosity of lignin-modified binders was observed. This finding led to further research, incorporating Sasobit as a viscosity-reducing agent in the bitumen.

7.3.5 Mix Design

The design of asphalt mixtures is the foundation of pavement engineering, aimed at achieving durability, stability, and optimal performance under diverse traffic loads and environmental conditions. Over decades, various mix design methods have been developed, each catering to specific requirements. One of the most widely used methods is the Marshall mix design. This method focuses on creating a durable mix with an optimal air void content, generally around 4 %, while minimizing asphalt binder use to ensure good rutting resistance. Another notable approach is the Hveem mix design, which prioritizes stability, cohesion, and durability by ensuring adequate binder coating on aggregates to promote long-term performance. The Superpave (Superior Performing Asphalt Pavement) method represents a performance-driven approach. It integrates the selection of performance-graded (PG) asphalt binders and aggregates with compaction using the Superpave Gyratory Compactor (SGC). Superpave evaluates mix properties under targeted traffic and environmental conditions, using compaction effort levels (McGennis et al., 1995; Roberts et al., 2002).

The LC (*Laboratoire des Chaussées*) Method, developed by Quebec's MTMD (*Ministère des Transports et de la Mobilité Durable*), has a hybrid approach, incorporating elements of both the Superpave and the LCPC (*Laboratoire Central des Ponts et Chaussées*) methods. One of the significant distinctions of the LC method is its reliance on the volume of effective binder (V_{be}) for calculating the binder content, rather than the commonly used voids in mineral aggregate (VMA) and voids filled with asphalt (VFA). The LC method's main features include setting the V_{be} according to the specific type of mixture to be designed and optimizing the aggregate grading to meet air voids specifications (V_a) at a given level of compaction energy. This volumetric approach ensures the mix achieves the desired performance and durability characteristics.

The mix design process for WMA is fundamentally the same as that for HMA including aggregate gradation, binder content, and performance evaluations, except for lower construction temperatures (Haopeng Wang, Liu, Apostolidis, & Scarpas, 2018b). In most cases, WMA technologies, such as Sasobit, are incorporated into the mix without altering the core design parameters used in conventional HMA (Shiva Kumar & Suresha, 2019). The standard method for determining the construction temperatures of HMA is the equi-viscous (EQ) method, based on the guideline of ASTM D2493 standard and LC 25-007 test method (N. Liu, Liu, Li, & Sun, 2024). This method relies on measuring the viscosity of the binder using results from the Brookfield Rotational Viscometer (BRV) test. However, it is well established among researchers that the EQ method is not suitable for asphalt mixtures produced with modified binders, such as polymer-modified and warm mix-modified asphalt binders, as it often results in unrealistically high temperatures (Z. Chen, Zhang, Duan, & Shi, 2021; Ghuzlan & Al Assi, 2017; Haopeng Wang, Liu, Apostolidis, & Scarpas, 2018a). This limitation has led to widespread recognition that viscosity-based methods are less effective in evaluating WMA, as several studies have confirmed their insensitivity to WMA technologies (Bennert, Reinke, Mogawer, & Mooney, 2010; Gudimettla, Cooley, & Brown, 2003; Mo, Li, Fang, Huurman, & Wu, 2012; C. Wang et al., 2013). As a result, several alternative methods have been proposed to overcome the limitations of the EQ method for WMA mixtures. Among these alternative methods, the most prominent include the analogy, the phase angle, the CEI & TDI, and the air voids methods (Sukhija & Saboo, 2021). Between those, the air voids method has emerged as the most reliable and widely used approach for determining WMA construction temperatures (W. Wang, Cheng, Sun, Sun, & Liu, 2022). The air voids method determines construction temperatures by evaluating the compaction behavior of asphalt mixes at various temperatures. This approach involves measuring the air voids content at different compaction temperatures and selecting the temperature at which the desired air voids level, typically the same as that of a reference mix, is achieved.

In summary, the introduction of bio-based additives like lignin, along with advanced technologies such as WMA and Sasobit, represents a significant step forward in the pursuit of more sustainable road construction practices. By lowering construction temperatures, reducing energy consumption, and decreasing reliance on petroleum-based binders, these innovations contribute to environmental sustainability, reducing the ecological impact of road construction.

7.4 Experimental campaign

In this study, asphalt mixes were prepared using varying proportions of Kraft lignin and Sasobit. The preparation, design, testing, and evaluation of these mixes were carried out to assess their volumetric and mass properties, with a focus on the effects of these materials on construction temperatures. The following sections provide objectives and scope, details on the materials used, mix compositions, and the methodologies employed for testing.

7.4.1 Objective and Scope

The objective of this research is to investigate the novel idea of incorporating Sasobit, a WMA additive, into lignin-modified asphalt mixes. More specifically, this study aims to investigate the individual and combined use of Kraft lignin and Sasobit in asphalt mixes to evaluate the volumetric and mass properties and address challenges related to construction temperatures.

This study focuses on two sustainable approaches: first, the utilization of Kraft lignin in asphalt mixes to reduce environmental impact; and second, the reduction of construction temperatures of lignin-modified mixes, which results in decreased fuel consumption, energy use, and emissions. Combining these two approaches, the study aims to determine whether the addition of Sasobit can effectively compensate for the increased construction temperatures caused by Kraft lignin, thereby enabling a more sustainable and efficient asphalt production process. Key questions addressed in this research include whether Sasobit can mitigate the negative effects of lignin on construction temperatures and how these two materials interact in an asphalt mix in terms of volumetric properties. Additionally, the study aims to understand the role of Kraft lignin within the mix — whether it behaves more like a binder or a filler. The challenge is to develop an optimized mix design that incorporates both materials while achieving desired performance outcomes.

The scope of this study covers mix design formulation, assessment of volumetric and mass properties, and the analysis of compaction test results using the Superpave Gyratory Compactor (SGC). The study also evaluates the construction temperatures required for each mix while maintaining a consistent air voids content, a crucial parameter in asphalt mix performance and sustainability. The findings are expected to provide valuable insights into the behavior of Kraft lignin and Sasobit in asphalt mixes, the optimal mix design strategies for incorporating these materials, and the potential for reducing construction temperatures. The overall goal is to contribute to the development of more sustainable infrastructure by optimizing asphalt mix designs with innovative materials.

7.4.2 Materials

Four distinct types of aggregates were used for the asphalt mix, including 5-10 mm, 0-5 mm washed and 0-5 mm non-washed aggregates, and limestone filler. To determine the physical properties of these aggregates, various tests were conducted. The specific gravity and water absorption tests were performed on all aggregate types according to Quebec's LC 21-065, LC 21-066, and LC 21-067 test methods. Sieve analyses were also carried out in accordance with Quebec's LC 21-040 test method. Each test was conducted with two replicas (n = 2) to ensure the reliability of the results. The sampling of aggregates from the quarry followed Quebec's LC 21-010 test method, ensuring that the material was representative of the source. For testing and subsequent use in asphalt mixes, aggregate samples were reduced using a splitter, following Quebec's LC 21-015 test method. The detailed properties of the aggregates are shown in Table 7.1.

Table 7.1 Properties of aggregates

	Sieve size (mm)	Aggregate Type and Class			
		Stone ^{L} 5-10 mm	Stone ^{L} 0-5 mm W.	Sand 0-5 mm N.W.	Filler ^{L} 0-315 µm
Sieve analysis (% passing by mass)	28	100	100	100	100
	20	100	100	100	100
	14	100	100	100	100
	10	85	100	100	100
	5	8	97	98	100
	2.5	3	58	75	100
	1.25	2	27	56	100
	0.630	2	12	43	100
	0.315	2	9	34	99
	0.160	2	7	27	93
	0.080	1.7	6.2	21.2	79.0
Bulk specific gravity (G_{sb})		2.706	2.688	2.701	2.700
Apparent specific gravity (G_{sa})		2.752	2.758	2.758	2.775
Water Absorption (%)		0.61	0.95	0.77	1.00
^{L} Limestone W.: Washed N.W.: Non-Washed					

The Kraft lignin used in this study (Figure 7.1a) was obtained from FPInnovations in Canada. The product is extracted from softwood and is provided as a fine, sticky brown powder.

Additionally, it has been investigated in previous laboratory studies (Al-falahat et al., 2024; Lamothe et al., 2024; Lamothe et al., 2022; Rezazad Gohari et al., 2023, 2024). The particle size distribution analysis revealed that the particle size ranged between 1 and 100 µm, with 80 % of the particles falling between 5.47 and 48.7 µm. Additionally, the Kraft lignin has a density of 1.2–1.3 g/cm³ and a potential of hydrogen (pH) ranging from 3 to 4. More details regarding its properties are available in our earlier publications (Rezazad Gohari et al., 2023, 2024).

Sasobit, a long-chain aliphatic hydrocarbon wax, was used (Figure 7.1b) in this study. The Sasobit used was sourced from Sasol Wax in South Africa. According to the manufacturer's recommendation, optimal results are achieved with a 3 % addition of Sasobit by weight of the bitumen. This amount can significantly lower the maximum construction temperatures required for asphalt mixes (SasolChemicals, 2025).

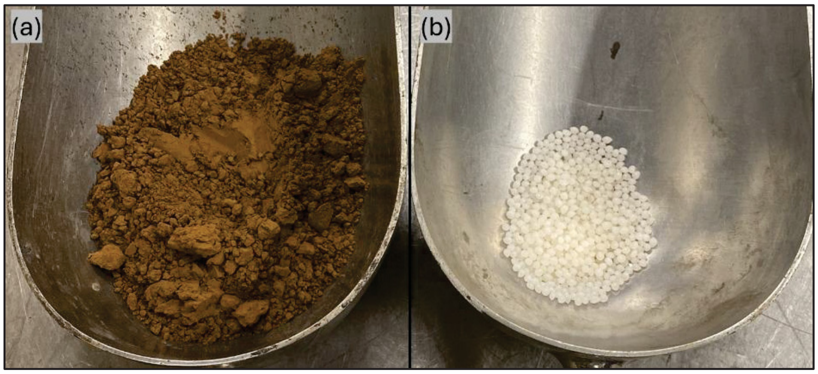


Figure 7.1 Materials used in this study: (a) Kraft lignin and (b) Sasobit

In this study, an unmodified PG 58S−28 bitumen was utilized. This bitumen grade is suitable for standard (S) traffic levels and cold climates in Montreal area (Canada). Due to the manufacturer’s specification sheet, this bitumen has a flashpoint of 273 °C (ASTM D 92), and a density of 1.021 g/cm³ at 25 °C (AASHTO T 228). Other notable properties include storage stability of 0.3 °C (LC 25-003), an ash content of 0.28 % (ASTM D 8078), and a $|G^*|/\sin(\delta)$ value of 1.54 kPa at 58 °C, as per AASHTO T 315.

According to our previous study (Rezazad Gohari et al., 2024) a comprehensive evaluation of the viscosity properties of this bitumen and its modified versions incorporating Kraft lignin and/or Sasobit was conducted. The viscosity of the bitumen samples was determined using the BRV test, following the LC 25-007 Quebec test method. Four selected results from that study are utilized in the application of the EQ method including virgin bitumen (VB) as a reference (REF), bitumen modified with 20 % Kraft lignin (20L), bitumen modified with 3 % Sasobit (3S), and a combined system of bitumen modified with 20 % Kraft lignin and 3 % Sasobit (20L3S). The viscosity measurements of these samples are detailed in Table 7.2.

Table 7.2 Viscosity test results for VB (REF), 20L, 3S, and 20L3S bitumen samples

Code	Viscosity (mPa·s)	
	At 135 (°C)	At 165 (°C)
VB (REF)	305	86
20L	568	166
3S	254	76
20L3S	404	128

7.4.3 Asphalt mixes

In this study, an ESG-10 (*Enrobé Semi-Grenu*) asphalt mix – a surface mix with a nominal maximum aggregate size (NMAS) of 10 mm – was chosen in accordance with MTMD standard 4202. To evaluate the effects of Kraft lignin and Sasobit on the properties of asphalt mixes, four distinct mixes/samples were prepared. These mixes include both HMA and WMA variants, each with varying contents of Kraft lignin and Sasobit. The HMA samples include a reference mix (HMA-REF), and a mix modified with 20 % Kraft lignin (HMA-20L). The WMA samples consist of a mix with 3 % Sasobit (WMA-3S) and a mix with both 20 % Kraft lignin and 3 % Sasobit (WMA-20L3S). Table 7.3 summarizes the composition and coding of each sample throughout the study.

Table 7.3 Composition and coding of asphalt mixes

Mix description	Kraft lignin (wt%) [1]	Sasobit (wt%) [2]	Code
Hot Mix Asphalt (HMA)	0	0	HMA-REF
	20	0	HMA-20L
Warm Mix Asphalt (WMA)	0	3	WMA-3S
	20	3	WMA-20L3S

[1] The Kraft lignin content is a percentage of the total binder weight (considering Kraft lignin as 100 % binder).

[2] Sasobit content is expressed as a percentage of the total binder weight.

7.4.4 Mix Design

The LC method was employed for the mix design, emphasizing a volumetric approach to optimize binder content and achieve target air voids (V_a) under specified compaction energy levels. This method ensures that the volume of the effective binder (V_{be}) for ESG-10 meets a minimum value of 12.2 %. The Va requirements with the Superpave Gyratory Compactor (SGC) are defined as follows: greater than 11 % at 10 gyrations, between 4 and 7 % at 80 gyrations (N_{design}), and above 2 % at 200 gyrations. Gradation requirements are provided in the next section (7.4.4.1).

7.4.4.1 Reference Hot Mix Asphalt (HMA-REF)

The HMA-REF serves as a baseline to evaluate the performance and characteristics of modified asphalt mixes. The mix design process followed the requirements for gradation to meet control points (Figure 7.2), ensuring compliance with the mix design method. Once the gradation was finalized, the bitumen content was determined to achieve a fixed V_{be} as per the requirements. This V_{be} was verified using the theoretical maximum specific gravity (G_{mm}). Following that, SGC tests were conducted to ensure adequate compactability of the mix. The final mix design selected for the HMA-REF utilized a total binder content of 5.67 % of the total weight of the asphalt mix (V_{be} required of 12.2 %). Figure 7.2 shows the detailed particle size distribution for the targeted mix and Table 7.4 represents the proportion (%) of each material in the HMA-REF mix.

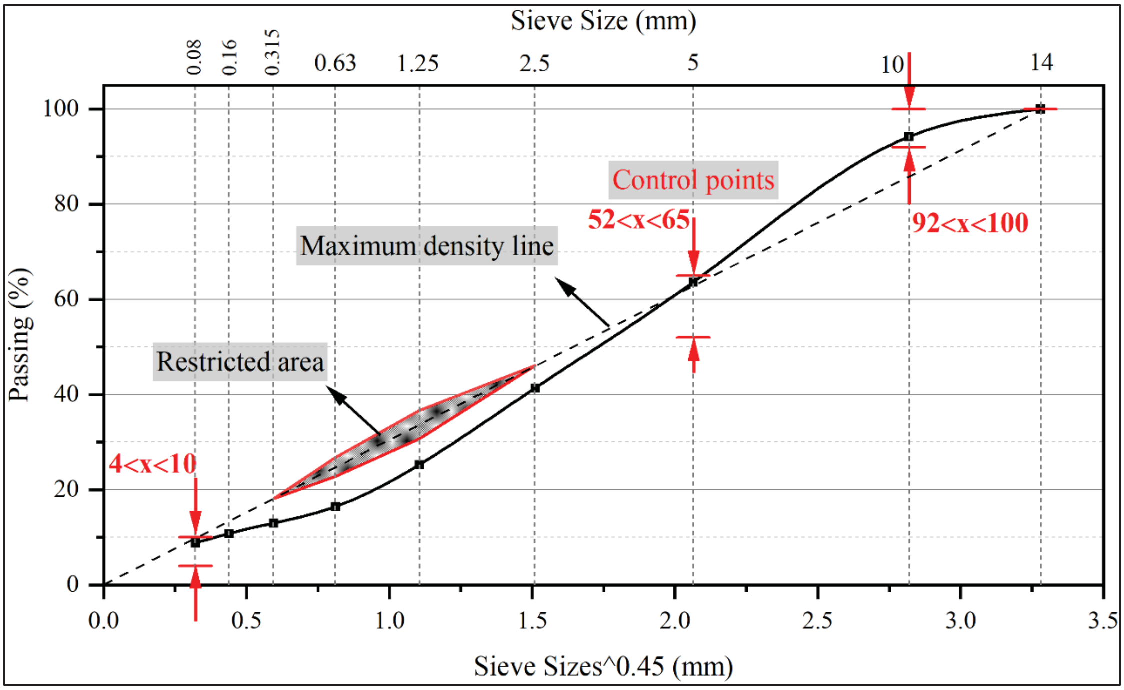


Figure 7.2 Particle size distribution of all asphalt mixes with requirements of MTMD standard 4202

Table 7.4 Proportion of binder and aggregates in HMA-REF

Proportion of materials in HMA-REF (%)	
Binder (P_b)	5.67
5-10 mm	35.84
0-5 mm W.	34.91
0-5 mm N.W.	22.64
Filler	0.94
W.: Washed; N.W.: Non-Washed.	

7.4.4.2 Methodology to Determine the Construction Temperatures

For HMA-REF and HMA-20L mixes, the EQ method was used to establish the mixing and compaction temperatures. However, for the WMA-3S and WMA-20L3S mixes, it became clear that the EQ method was not effective. While the EQ method was initially applied to determine the construction temperatures, the temperatures were subsequently adjusted based on the air voids content. The temperatures were modified until the air voids content matched the reference mix. This continuous process helped determine the construction temperatures at which the air voids were the same as the reference mix.

7.4.4.3 Modified Mixes with Kraft Lignin and Sasobit

In the LC mix design method, the specific gravity of the binder (G_b) plays a crucial role in formulating the mix design. One of the critical considerations in this process is how to accurately account for the impact of Sasobit and Kraft lignin, given their distinct properties in the asphalt mix. Possible approaches for integrating Kraft lignin into the mix can be considered: (1) as a binder substitute, (2) as a filler, or (3) as a hybrid, where Kraft lignin serves as both binder and filler in varying proportions. A similar approach was adopted for Sasobit, where it was considered both as a binder substitute and an additive in different configurations.

Upon evaluating these scenarios, it was determined that both Kraft lignin and Sasobit would be treated as replacements for bitumen in the binder composition for mix design calculations, enabling the same volume of binder to be used in the mixtures. This required calculating the G_b of the binder by incorporating the proportion of these materials, as outlined in Equation 7.1.

$$G_b = \frac{\Sigma P_n}{P_1/G_1 + P_2/G_2 + \dots + P_n/G_n} \qquad \text{Equation 7.1}$$

Where P_n is the proportion (by mass) of each component in the binder, and G_n is the specific gravity of each corresponding component. Following the calculations, the results are summarized in Table 7.5, showing the G_b value and the binder composition for each mix, which are directly influenced by the varying proportions of Kraft lignin and Sasobit. For the HMA-REF mix, which contains only bitumen, the G_b remains at 1.024, reflecting the typical specific gravity of unmodified bitumen. In the HMA-20L mix, the incorporation of 20 % Kraft lignin increases the G_b to 1.065, attributed to the higher specific gravity of Kraft lignin (1.267). Conversely, in the WMA-3S mix, the addition of 3 % Sasobit, with its lower specific gravity (0.592), reduces the G_b to 1.002. The WMA-20L3S mix, which incorporates both 20 Kraft lignin and 3 % Sasobit, results in a G_b of 1.041, reflecting the combined influence of both materials on the binder's composition and properties. These values are crucial for accurately understanding the behavior of the modified mixes, as the G_b directly affects the overall volumetric properties of the asphalt mix.

Table 7.5 Calculated specific gravity and binder composition for all mixes

Material	Specific gravity at 25 °C (unitless)	Binder composition (% by mass)			
		HMA-REF	HMA-20L	WMA-3S	WMA-20L3S
Bitumen	1.024	100	80	97	77
Kraft lignin	1.267	0	20	0	20
Sasobit	0.592	0	0	3	3
Binder (G_b) calculated with Equation 7.1		1.024	1.065	1.002	1.041

The variation in binder content of the four mixes is primarily due to the inclusion of Kraft lignin and Sasobit. In the HMA-20L mix, the binder content increased to 5.82 %, compared to 5.67 % in the HMA-REF mix. This increase is necessary to compensate for the higher specific gravity of Kraft lignin (1.267) compared to bitumen (1.024), ensuring consistent volumetric properties across the mixes. Similarly, in the WMA-3S mix, the binder content was reduced to 5.50 %, reflecting the addition of 3 % Sasobit, which has a much lower specific gravity (0.592).

In the WMA-20L3S mix, the combination of 20 % Kraft lignin and 3 % Sasobit required a reduction in binder content to 5.63 %.

7.4.5 Preparation of samples

The addition of Kraft lignin and Sasobit to bitumen can significantly alter its viscosity, directly impacting the mixing and compaction processes. Therefore, before producing the asphalt mixes, it is crucial to determine the mixing and compaction temperatures for all the mixtures. The Superpave system recommends specific viscosities for optimal mixing and compaction, with target values of 0.17 ± 0.02 Pa·s for mixing and 0.28 ± 0.03 Pa·s for compaction. These temperatures are usually determined by evaluating the viscosity at two standard temperatures of 135 and 165 °C, using the BRV test.

As mentioned previously, viscosity measurements of the four bitumen samples — VB (REF), 20L, 3S, and 20L3S — were conducted (Table 7.2). Using these viscosity values, each sample's corresponding mixing and compaction temperatures were calculated and are presented in Table 7.6.

Table 7.6 Mixing and compaction temperatures of VB (REF), 20L, 3S, and 20L3S bitumen samples using BRV test results and EQ method

Code	Calculated*	
	T_{mixing} (°C)	$T_{compaction}$ (°C)
VB (REF)	148^{0}	137^{0}
20L	164^{+16}	151^{+14}
3S	144^{-4}	133^{-4}
20L3S	157^{+9}	144^{+7}
* Superscript value: temperature difference with REF bitumen.		

It is important to note that in this study, the dry mixing process (dry method) was used by adding both Kraft lignin and Sasobit directly into the mixes, and the following protocol was implemented to ensure the proper incorporation of all materials. Given the requirement to heat all components to the target mixing temperature, an additional 15 °C was applied to compensate for heat loss during mixing, as per the LC 26-003 Quebec test method. Special consideration was given to the Kraft lignin, which contained 2.6 % moisture (Al-falahat et al., 2024). Initially, heating the Kraft lignin for one hour was attempted to eliminate moisture. However, a preliminary lab test revealed that this process caused odor emission, darkening of the Kraft lignin, and the formation of clumpy masses, which prevented proper mixing with the aggregates and bitumen. As a result, the Kraft lignin was used at room temperature during the mixing process. For the HMA-20L mix, after adding Kraft lignin to the aggregates, it was manually blended with the aggregates in the mixing bowl using a spoon for a few seconds before adding the bitumen. This step was deemed necessary after visual observations indicated that it helped achieve a more uniform distribution of the Kraft lignin throughout the aggregate matrix. This ensures better interaction between the Kraft lignin, aggregates, and bitumen during mixing. In the WMA-3S mix, Sasobit prills were directly added to the bitumen after it was added to the aggregates. This approach is critical for lowering the binder's viscosity effectively. Adding Sasobit directly to the aggregates in advance would cause rapid melting, reducing its impact on the viscosity of the bitumen. For the WMA-20L3S mix, a combination of the processes used for the HMA-20L and WMA-3S mixes was implemented, as shown in Figure 7.3. This protocol might be an effective procedure for this type of mixer (countertop mixer: Hobart model A200). For mixers equipped with heating systems, this might yield even better results.

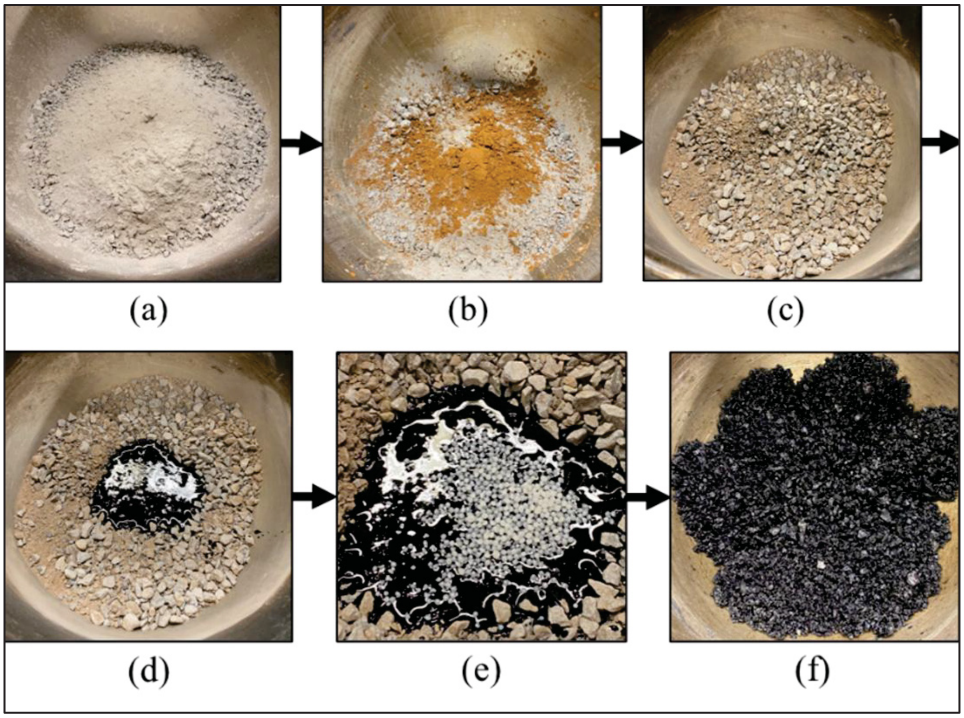


Figure 7.3 Mixing protocol of mix containing lignin and Sasobit (WMA-20L3S): (a) adding aggregates, (b) adding Kraft lignin, (c) mixing aggregates and Kraft lignin, (d) adding bitumen, (e) adding Sasobit prills and, (f) mixing all materials with a mechanical mixer

Following the mixing process, the loose asphalt mixes were cured at the compaction temperature for two hours, as specified by the LC 26-003 Quebec test method. This curing process allows sufficient time for the aggregates to absorb the binder and better simulates in-situ conditions, ensuring more representative test results. To ensure proper coating and uniform distribution of the binder, visual inspections were conducted before and after curing to ensure the aggregates were fully coated. Adequate coating of the aggregates is essential for the asphalt mix's structural integrity and long-term durability.

7.4.6 Testing

7.4.6.1 Maximum Specific Gravity (G_{mm})

The maximum specific gravity (G_{mm}), also known as Rice density, is a crucial parameter in designing and analyzing asphalt mixtures. For HMA and WMA, the G_{mm} quantifies the maximum density that a specific mix can achieve. According to LC 26-045 Quebec test method, it is measured by weighing the loose asphalt mix (uncompacted) in air and in water (volumetric method with a glass container and a glass plate). Accurate determination of G_{mm} is vital for subsequent volumetric property calculations of the mix (average of two replicates: $n = 2$).

7.4.6.2 Superpave Gyratory Compactor (SGC)

The SGC is a crucial device used to compact asphalt mixtures in the laboratory, simulating the compaction that occurs in the field during pavement construction. This test is essential for evaluating key properties of asphalt mixtures, such as bulk density (G_{mb}), air voids content (V_a), and the compaction curve (gyration number versus V_a). During the SGC test, the device applies a vertical pressure of 600 kPa while simultaneously rotating the sample at an angle of 1.16 degrees. The compaction is performed at a rate of 30 gyrations per minute with specific numbers of gyrations selected to simulate various compaction levels. For ESG-10 HMA, the gyration levels are 10 ($N_{initial}$), 80 (N_{design}), and 200 (N_{max}), corresponding to N_{10}, N_{80}, and N_{200}, respectively.

The SGC accommodates two mold sizes of 150 and 100 mm. The 150 mm mold is more commonly used, especially for asphalt mixes containing large aggregates, although it requires a greater quantity of material compared to the smaller mold. Due to the limited availability of materials for this study, a 100 mm mold was used. To ensure that the air voids content of these smaller samples aligns with the requirements of the LC mix design method, additional tests were performed using the standard 150 mm mold. This approach was implemented to provide a comparative analysis and allow the determination of a conversion factor for adjusting the air voids content results from the 100 mm mold to those of the 150 mm mold. Consequently, tests were conducted on both 100 and 150 mm molds for the HMA-REF and HMA-20L samples. The SGC tests were conducted in accordance with the LC 26-003 Quebec test method. Each mix was tested at least three times (average of n = 3) to ensure the repeatability and reliability of the results.

7.4.6.3 Volumetric and mass properties

The evaluation of volumetric and mass properties is essential for understanding the overall behavior, durability, and performance of asphalt mixtures. These properties provide insights into the interaction between aggregates, binder, and additives, playing a critical role in determining the compaction, stability, and longevity of the asphalt pavement. Since aggregates are the largest portion of the asphalt mix, they have a significant influence on the engineering properties of the asphalt mix (Al-Bayati, Tighe, & Achebe, 2018). Here, various volumetric and mass properties were examined such as the maximum specific gravity (G_{mm}), binder absorbed by the aggregate (V_{ba}, P_{ba} and M_{ba}), air voids content (V_a), volume of effective binder (V_{be}), voids in mineral aggregate (VMA), and voids filled with asphalt binder (VFA), mass of effective binder (M_{be}) and mass of aggregate (M_{agg}) etc. are also analyzed to capture the overall volume and mass distributions within the mix. Figure 7.4 shows the terminology of volumetric and mass properties for the components of a compacted asphalt mix.

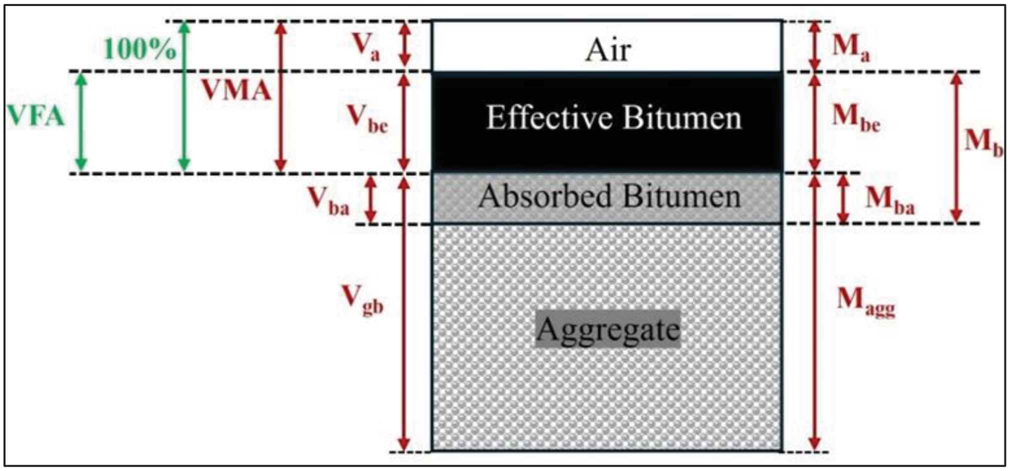


Figure 7.4 Volumetric and mass components of a compacted asphalt mix

7.5 Test Results and Discussion

7.5.1 SGC test results

In this study, the majority of SGC tests were performed using 100 mm molds due to material limitations. However, 150 mm molds are typically employed in standard practices, as they provide a more representative evaluation of mix performance, especially for mixes with larger aggregates. To ensure the results from the 100 mm molds align with the requirements of the LC mix design method, it was essential to determine a conversion factor. This factor facilitates the accurate interpretation and comparison of results between the two mold sizes. The subsequent subsections detail the determination of this conversion factor and the influence of Kraft lignin on the compactability of asphalt mixes.

7.5.1.1 Conversion factor for air voids content between 100 and 150 mm molds

The SGC test results for the 100 and 150 mm molds for HMA-REF and HMA-20L mixes are presented in Table 7.7.

Table 7.7 Air voids content and conversion factors of HMA-REF and HMA-20L mix using 100 and 150 mm molds at different gyration levels

Gyration (#: term)	Designation (N_i)	Air void (%) HMA-REF *		Conversion Factor **	Air void (%) HMA-20L*		Conversion Factor **
		100 ***	150 ***		**100 *****	150 ***	
10: N_{10}	$N_{initial}$	**16.21**	14.69	0.91	**16.15**	14.77	0.91
80: N_{80}	N_{design}	**6.27**	5.43	0.87	**6.12**	5.74	0.94
200: N_{200}	N_{max}	**2.91**	2.62	0.90	**3.20**	3.25	1.02

* Compaction temperatures of 137 °C for HMA-REF and 151 °C for HMA-20L mixes.
** Conversion factor: % air voids with 150 mm mold / % air voids with 100 mm mold.
*** Mold diameter in mm.

The analysis of these results revealed a conversion factor of 0.9, which was determined to adjust the air voids content from a 100 mm mold to a 150 mm mold for both HMA-REF and HMA-20L asphalt mixes. The differences in air voids content are due to variations in stress distribution and particle arrangement during compaction (Dubois, De La Roche, & Burban, 2010). While both molds receive the same compaction energy — pressure of 600 kPa combined to gyration number (1 to 200) — the larger diameter of the 150 mm mold allows for more even stress distribution and better particle packing. This leads to fewer air voids compared to the 100 mm mold, which has a higher surface-to-volume ratio, resulting in more voids around and within the sample. Consequently, the 150 mm mold achieves a denser structure. Using the conversion factor of 0.9, the air voids content measured in the 100 mm mold was correctly aligned with the requirements of the LC mix design method. As a result, the adjusted air voids content was confirmed to meet the specified ranges of >11 % at N_{10}, 4–7 % at N_{80}, and >2 % at N_{200}, ensuring compliance with the mix design criteria. Based on the assumption that the WMA-3S and WMA-20L3S mixes exhibit similar behavior, the same conversion factor of 0.9 was applied to verify compliance with the mix design criteria for these mixes as well. This demonstrates the effect of mold size on compaction efficiency and air voids distribution.

7.5.1.2 Kraft lignin Behavior on Compactability of Asphalt Mixes

An in-depth analysis of the data highlights the impact of Kraft lignin on the asphalt mix and clarifies its role within the mixture. The test results show that both HMA-REF and HMA-20L have similar air voids conversion factors (Table 7.7) at lower gyration levels (N_{10}), but the differences become more pronounced at higher compaction levels (N_{80} and N_{200}). This suggests that the presence of Kraft lignin in the HMA-20L mix impacts the compaction characteristics.

Indeed, at a low gyration level (N_{10}), both HMA-REF and HMA-20L show similar conversion factors of 0.91. This suggests that, at the early stages of compaction, the presence of 20 % Kraft lignin in the HMA-20L mix does not significantly alter the air voids distribution compared to the HMA-REF mix. Both mixes behave similarly under initial compaction stresses. At higher gyrations (N_{80} and N_{200}), the HMA-20L mix with Kraft lignin shows higher conversion factors with 0.94 at N_{80} and 1.02 at N_{200}, compared to the HMA-REF mix, which has conversion factors of 0.87 at N_{80} and 0.90 at N_{200}. A higher conversion factor indicates that the air voids content is higher and the material achieves less compaction in the 150 mm mold.

The increased air voids in the HMA-20L mix at higher gyration levels, compared to HMA-REF, can be attributed to the presence of Kraft lignin, despite the fact that the compaction temperature was increased by 14 °C (151 vs 137 °C). This behavior could be linked to the increased viscosity of the binder due to the addition of Kraft lignin, or the partial role of Kraft lignin acting as a filler. Although this filler effect might help to fill voids between aggregates, the increased viscosity likely hinders effective compaction by reducing the mobility and rearrangement of particles within the mix, thereby reducing the compactability of the HMA-20L.

This dual effect—where Kraft lignin functions both as a binder replacement and a filler—complicates the compaction dynamics. This highlights the complex interplay of factors introduced by Kraft lignin in the compaction process of asphalt mixes.

7.5.2 Determination of Optimal Construction Temperatures

To determine the optimal construction temperatures for the asphalt mixes while achieving consistent air voids content, the following steps were conducted. The first step involved conducting the SGC test on the HMA-REF as the reference mix. In this mix, the air voids at 10, 80, and 200 gyrations (N_{10}, N_{80}, and N_{200}) were considered the baseline values. The mixing and compaction temperatures for HMA-REF were determined based on the EQ method using the BRV test results (refer to section 7.4.5). As presented in Table 7.6, the mixing and compaction temperatures for this mix were set at 148 and 137 °C, respectively. Figure 7.6 shows the SGC test results for the HMA-REF mix, where the air voids at N_{10}, N_{80}, and N_{200} were 16.2, 6.3, and 2.9 %, respectively. For the HMA-20L mix, the same procedure was followed, with the mixing and compaction temperatures set at 164 and 151 °C, respectively. The air voids content for 10, 80, and 200 gyrations were 16.1, 6.1, and 3.2 %, which are nearly identical to the reference mix.

As shown in Figure 7.5, for the WMA-3S mix, the initial construction temperatures were selected based on the BRV test results, which were 144 °C for mixing and 133 °C for compaction. As mentioned earlier, the EQ method does not apply to mixes containing Sasobit, so these temperatures were used as a starting point. At these initial temperatures, the air voids content at N_{80} was 5.4 % (red curve: Figure 7.5a), which did not align with the reference mix, indicating that a reduction in temperature was necessary for mixes with Sasobit. Consequently, the temperatures were lowered to 133 and 122 °C. However, the air voids content at these temperatures (N_{80} = 5.9 %: blue curve in Figure 7.5a) still did not match the reference values. Further adjustments were made, setting the temperatures to 117 °C and 108 °C, which resulted in a significant increase in air voids content at N_{80}, reaching 8.2 % (green curve: Figure 7.5a). Through interpolation of the data, the optimal temperatures were determined to be 127 °C for mixing and 116 °C for compaction (grey curve: Figure 7.5a). At these optimized temperatures, the samples were produced, and air voids content were 16.2, 6.3, and 3.0 % for N_{10}, N_{80}, and N_{200}, respectively, matching the reference mix. Thus, the appropriate construction temperatures for the WMA-3S mix were successfully identified.

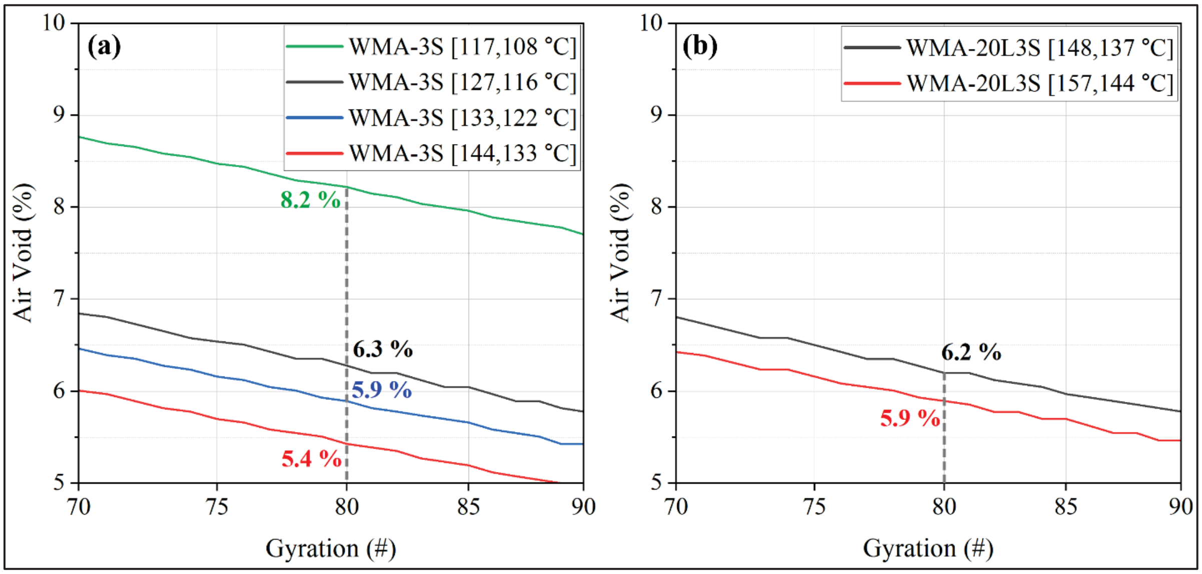


Figure 7.5 Air void content at 80 gyrations for: (a) WMA-3S and, (b) WMA-20L3S mixes at varying construction temperatures [T_{mixing}, $T_{compaction}$]

For the final mix, WMA-20L3S, the initial construction temperatures were set based on the BRV test results, which indicated 157 °C for mixing and 144 °C for compaction. The air voids content at these temperatures did not match the reference mix (N_{80} = 5.9 %: red curve), as shown in Figure 7.5b. Given the findings from the WMA-3S mix, it was evident that the EQ method is not accurate for mixes containing Sasobit, requiring a reduction in temperatures. When the construction temperatures were reduced to 148 °C for mixing and 137 °C for compaction (grey curve: Figure 7.5b), the air voids content for the WMA-20L3S mix was 16.2, 6.2, and 3.2 % for N_{10}, N_{80}, and N_{200}, respectively, which closely matched the HMA-REF mix and met the target air voids requirements. It is important to note that changes in mixing temperatures lead to slight variations in the calculated binder content (P_b) due to their impact on the measured G_{mm}. These changes must be carefully considered when recalculating mix proportions to ensure compliance with the target volumetric requirements. The final air voids content for all mixes are presented in Figure 7.6.

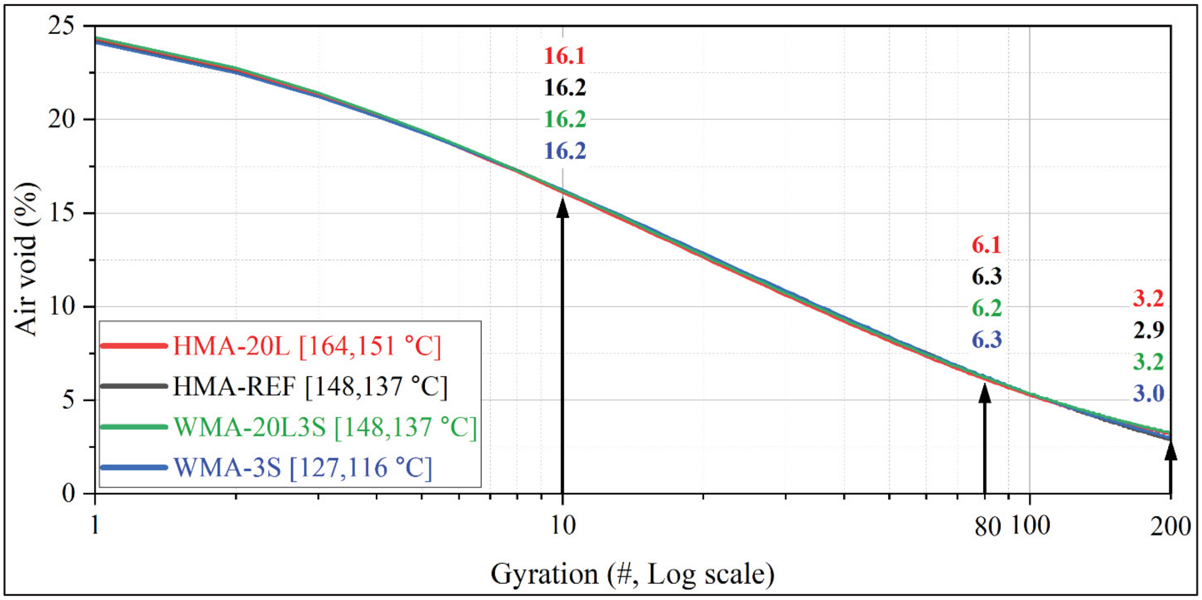


Figure 7.6 Final air voids content at different gyrations for all mixes and related construction temperatures [T_{mixing}, $T_{compaction}$]

7.5.2.1 Binder Compositions and Final Construction Temperatures of Asphalt Mixes

After determining the optimal mixing and compaction temperatures to achieve consistent air voids content across all mixes, the final construction temperatures and binder compositions were identified as shown in Figure 7.7 and Figure 7.8.

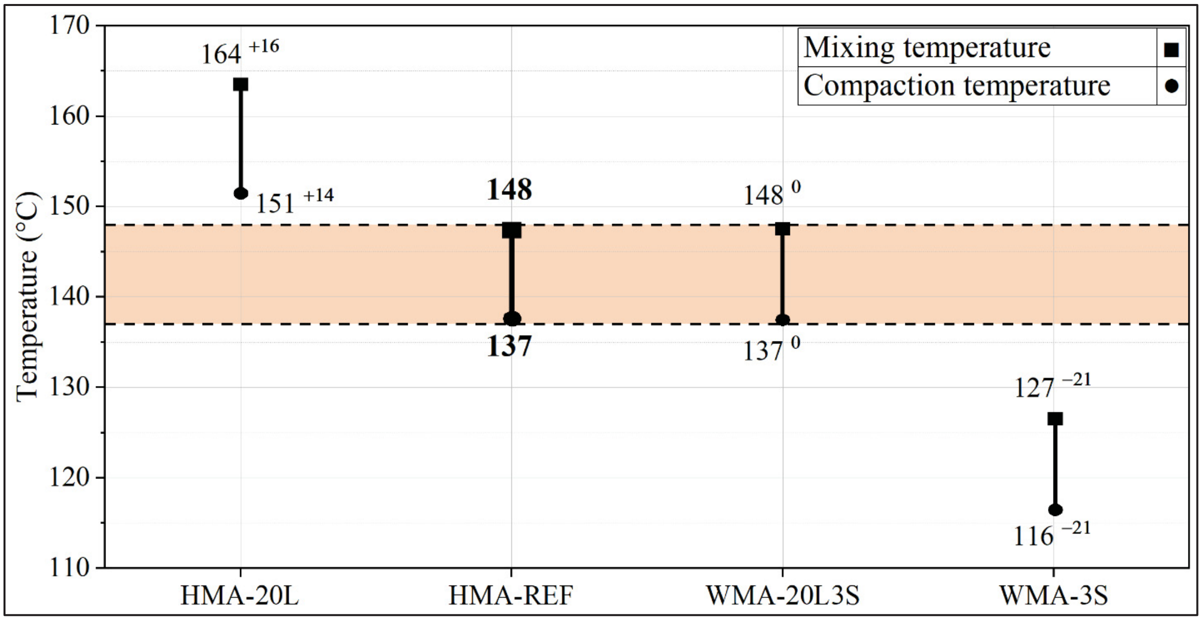


Figure 7.7 Final construction temperatures of all mixes (superscript value: temperature difference with HMA-REF)

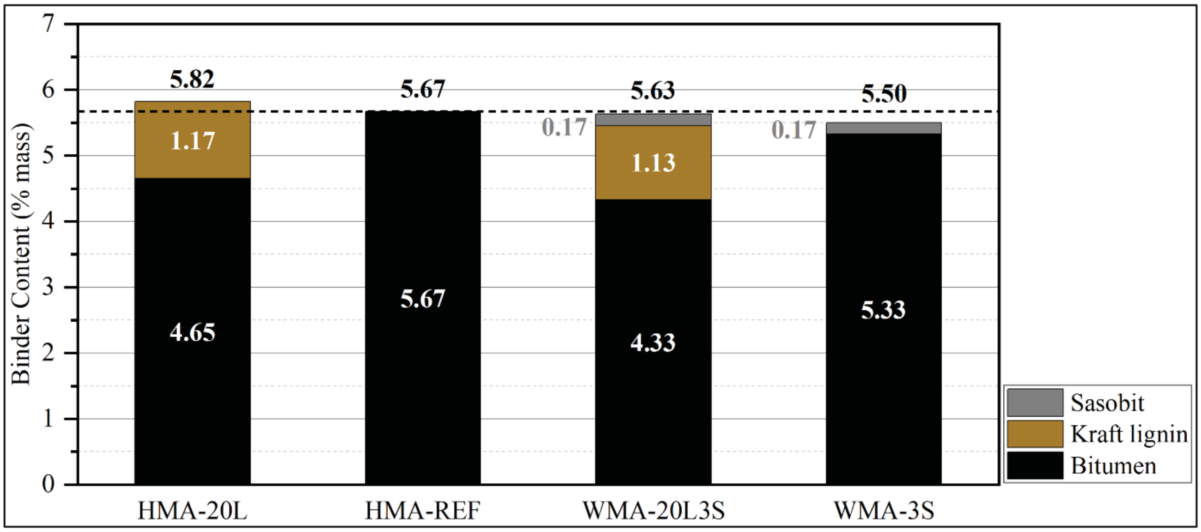


Figure 7.8 The final binder composition of all mixes

For the HMA-REF mix, the construction temperatures were set at 148 °C for mixing and 137 °C for compaction, with a binder content of 5.67 %, which consists entirely of bitumen.

In the HMA-20L mix, the inclusion of 20 % Kraft lignin led to an increase in construction temperatures. The mixing and compaction temperatures increased to 164 and 151 °C, respectively, representing an increase of 16 and 14 °C compared to the HMA-REF mix (Figure 7.7). The binder content for this mix is 5.82 %, comprising 4.65 % bitumen and 1.17 % Kraft lignin (% mass). It is notable that the addition of Kraft lignin reduced the bitumen content from 5.67 % in the HMA-REF mix to 4.65 % in the HMA-20L mix, a decrease of 1.02 % (Figure 7.8). This reduction in bitumen usage is significant and highlights the resource-saving potential of using Kraft lignin, despite the undesired increase in construction temperatures.

For the WMA-3S mix, the results show that mixing at 127 °C and compaction at 116 °C achieved the same air voids content as the HMA-REF mix (Figure 7.6). As expected, these lower construction temperatures align with the role of Sasobit in reducing viscosity and promoting workability at reduced temperatures. The temperatures were lowered by 21 °C for both mixing and compaction (Figure 7.7), consistent with findings from previous studies and the manufacturer's recommendations (SasolChemicals, 2025). The binder content in the WMA-3S mix was reduced to 5.50 %, with bitumen and Sasobit contents of 5.33 and 0.17 %, respectively (Figure 7.8). The decrease in bitumen content by 0.34 % compared to the HMA-REF mix represents a positive outcome, demonstrating the efficiency of using less bitumen.

The WMA-20L3S mix achieved construction temperatures identical to those of the HMA-REF mix — 148 °C for mixing and 137 °C for compaction (Figure 7.7). This result is particularly promising from a sustainability perspective. While the HMA-20L mix showed higher temperatures due to the presence of Kraft lignin, the addition of 3 % Sasobit in the WMA-3S mix successfully reduced the temperatures. The combination of these two materials in the WMA-20L3S mix led to a remarkable outcome as the Sasobit effectively offset the increase in construction temperatures caused by the 20 % Kraft lignin. This finding is valuable, as it suggests that Sasobit can mitigate the undesirable effects of Kraft lignin in terms of increased viscosity and higher construction temperatures. Another significant observation is the reduction in bitumen content when using both materials. The bitumen content in the WMA-20L3S mix dropped to 4.33 %, compared to 5.67 % in the HMA-REF mix, which is a reduction of 1.34 % (Figure 7.8). This substantial decrease in bitumen usage is highly desirable, as its reduction contributes to more sustainable pavement solutions.

To sum up, the addition of 3 % Sasobit to lignin-modified mixes (WMA-20L3S) proves to be an effective strategy for compensating for the increased construction temperatures associated with Kraft lignin, allowing the mix with 20 % Kraft lignin to achieve the same construction temperatures as the reference mix. Moreover, the combined use of Sasobit and Kraft lignin in asphalt mixes not only reduces the construction temperature but also significantly decreases the bitumen usage in the binder, further enhancing the sustainability of the mix.

7.5.3 Volumetric and Mass Analysis

The volumetric and mass properties of a compacted mix and understanding these parameters provide essential insights into the performance and durability of the mixtures. The detailed numerical values for all mixes are calculated and presented in Table 7.8. The analysis reveals several key observations regarding the behavior of the mixes.

Table 7.8 Volumetric and mass properties of all mixes

Parameters		HMA-20L	HMA-REF	WMA-20L3S	WMA-3S
Specific Gravity (---)	G_{mm} (n = 2)	2.515	2.511	2.510	2.507
	P_{ba} (n = 2) (% of aggregate)	0.69	0.74	0.60	0.66
	G_{se} (n = 2)	2.746	2.752	2.741	2.747
	G_{mb} ^{1} (n = 2)	2.361	2.353	2.354	2.350
Volumetric (%) ^{2}	V_a	6.1	6.3	6.2	6.3
	V_{be}	11.45	11.43	11.44	11.43
	$V_{be\_0\%Va}$ ^{3}	12.2	12.2	12.2	12.2
	VMA	17.57	17.71	17.64	17.71
	VFA	65.17	64.57	64.86	64.57
	V_{ba} (% of aggregate)	1.76	1.96	1.56	1.77
	V_{gb}	82.43	82.29	82.36	82.29
Mass (%) ^{2}	M_a	0.00	0.00	0.00	0.00
	M_{be}	5.17	4.97	5.06	4.88
	M_{ba} (% of total mass)	0.65	0.70	0.57	0.62
	M_b (P_b)	5.82	5.67	5.63	5.50
	M_{agg}	94.18	94.33	94.37	94.50

[1] G_{mb} at N_{design} (80 gyrations) from SGC results.
[2] Values calculated based on the G_{mb} obtained at N_{design} (80 gyrations), except for $V_{be\_0\%Va}$.
[3] V_{be} value was determined with the 0 % air voids (V_a).
V_a: Volume of air voids for 100 mm mold at N_{design} (80 gyrations).
V_{be}: Volume of effective binder.
VMA: Voids in Mineral Aggregate.
VFA: Voids Filled with binder.
V_{ba}: Volume of absorbed binder.
V_{gb}: Aggregate volume by bulk specific gravity.
M_a: Mass of air.
M_{be}: Mass of effective binder.
M_{ba}: Mass of absorbed binder.
M_b: Total Mass of binder.
M_{agg}: Mass of aggregate.

7.5.3.1 G_{mm} Test Results and Analysis

The G_{mm} is influenced by several factors, including binder type, the binder content (P_b), absorbed binder by the aggregates (P_{ba}), and the viscosity of the binder (El Sayed, 2012). Other variables, such as aggregate properties, gradation, and mixing conditions remain consistent across the mixes in this study. Generally, an increase in P_b, higher P_{ba}, and a greater specific gravity of the binder (G_b) will result in a higher G_{mm} value. In the case of the HMA-20L mix, despite a slight reduction in P_{ba} compared to the HMA-REF mix, the G_{mm} increased slightly due to the higher P_b of 5.82 % and the increased specific gravity of the binder resulting from the addition of Kraft lignin. In the WMA-3S mix, both P_{ba} and P_b were reduced, and the specific gravity of the binder also decreased, leading to a corresponding reduction in G_{mm}. For the WMA-20L3S mix, the combination of Kraft lignin and Sasobit resulted in a lower P_{ba} but nearly identical P_b value to that of the HMA-REF mix. While Sasobit reduced the specific gravity of the binder compared to the HMA-20L mix, it remained higher than that of the HMA-REF mix. As a result, the G_{mm} value for WMA-20L3S closely matched the reference mix (HMA-REF). This outcome, where the G_{mm} values for both the HMA-REF and WMA-20L3S mixes are essentially the same, is desirable for ensuring consistent mix performance.

7.5.3.2 Binder Absorption (P_{ba}) Test Results and Analysis

In asphalt mixes, the percentage of binder absorbed by the aggregate, known as P_{ba}, is a mass property that influences the performance and durability of the pavement. This parameter reflects the amount of bitumen absorbed into the aggregate pores by mass, affecting the effective binder content and the overall workability and compactability of the mix. Understanding the behavior of P_{ba} in different mixes is essential for optimizing the mix design, especially when incorporating materials like Kraft lignin and Sasobit. Figure 7.9 shows the test results of P_{ba} for all mixes.

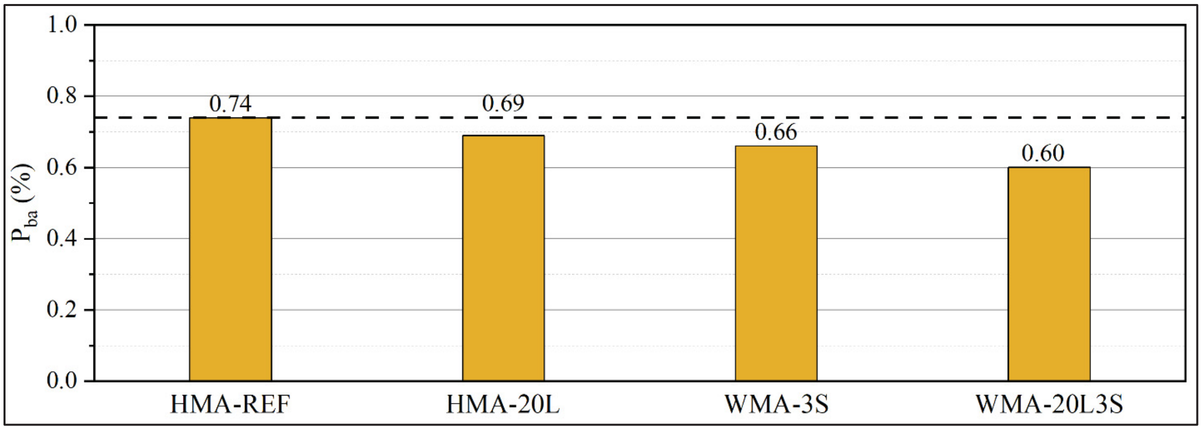


Figure 7.9 Percentage of binder absorbed by the aggregate (P_{ba}) for all mixes

The HMA-REF with 5.67 % P_b, results in a P_{ba} of 0.74 %. In the HMA-20L mix, the binder content is slightly increased to 5.82 % and test results show a decrease in P_{ba} to 0.69 %, which is lower than the reference mix (HMA-REF). Notably, the addition of 20 % Kraft lignin required an increase in construction temperatures to achieve the desired binder viscosity. Despite this increase, the binder absorption by the aggregates did not increase proportionally. The presence of Kraft lignin reduces binder absorption, which may be attributed to the complex structure of Kraft lignin with some elements acting as a filler, thereby preventing the aggregates from absorbing the binder.

For the WMA-3S mix, the binder content is 5.50 %, with significantly reduced construction temperatures. Test results indicate that P_{ba} decreased from 0.74 % in HMA-REF to 0.66 % in WMA-3S. This reduction in the absorbed binder may be due to the lower construction temperature or the reduced binder content, but the exact reasons require more research study.

The WMA-20L3S mix results in a binder content of 5.63 % with the same construction temperatures as the reference mix. Regarding P_{ba}, this mix exhibits the lowest binder absorption at 0.60 %, compared to the other mixes. When comparing WMA-20L3S to HMA-REF with the same construction temperatures, the lower bitumen content and the inclusion of both Kraft lignin and Sasobit contribute to the reduced P_{ba}. Similar to the HMA-20L mix, a portion of the Kraft lignin potentially acts as a filler, reducing binder absorption, while the reduced bitumen content in WMA-20L3S further lowers the P_{ba}.

In short, the reduction of P_{ba} in the asphalt mix may be beneficial as it enhances the availability of effective binder, improving the durability, workability, and compaction of the mix. This also leads to cost efficiency by reducing the required binder content. However, it’s important to note that Kraft lignin does not act entirely as a binder; instead, a portion of it functions as a filler, preventing the binder from penetrating the aggregates. Maintaining an optimal balance is crucial to ensure adequate interaction between the binder and aggregates, preventing potential issues like stripping or insufficient bonding.

7.5.3.3 Analysis of Additional Volumetric and Mass Properties

For volumetric parameters, the air voids (V_a) were maintained nearly identical, and the effective binder volume (V_{be}) remained identical, as intended during the design of the mixes. The VMA, which measures the voids space in the aggregate structure, also exhibited minimal variation across the mixes, confirming the uniformity in aggregate gradation and compaction. These consistent values indicate that the design process effectively controlled the aggregate structure and binder content, maintaining the target values for all key volumetric parameters. For the VFA, slight deviations were observed. In the HMA-20L mix, the VFA was slightly higher due to the increased binder content (P_b) and slightly reduced air voids (V_a), resulting in more voids being filled with binder compared to the reference mix. In contrast, the WMA-3S mix exhibited a reduced binder content (P_b = 5.50 %) yet achieved a VFA similar to the reference mix. The reduced binder viscosity, owing to the Sasobit addition, facilitated better compaction and voids filling despite the lower binder content. The WMA-20L3S mix displayed similar behavior, with slight differences in VFA compared to the reference mix, demonstrating the effectiveness of the Sasobit in maintaining proper compaction and voids filling. The V_{gb} (Aggregate volume by bulk specific gravity) and M_{agg} (Mass of Aggregate) values were also almost identical across all mixes, confirming consistency in aggregate content.

In summary, the volumetric and mass properties of the mixes, particularly G_{mm}, P_{ba}, and VFA, indicate that the addition of Kraft lignin and Sasobit in varying proportions has a measurable impact on the binder absorption, effective binder content, and compaction. Notably, Kraft lignin does not act entirely as a binder; instead, a portion of it functions as a filler, preventing the binder from penetrating the aggregates. Despite these variations, the results demonstrate that the WMA-20L3S mix closely mirrors the performance of the reference mix (HMA-REF), maintaining key volumetric properties and meeting target performance levels.

7.6 Conclusion

This study evaluated the impact of incorporating Kraft lignin and Sasobit into asphalt mixtures, specifically focusing on their influence on compaction behavior, construction temperatures, and the volumetric and mass properties of the mixes. The findings reveal several important insights regarding the performance of these materials in sustainable asphalt production.

First, the SGC test results showed that the compactability of the HMA-20L mix was reduced compared to HMA-REF, as indicated by higher air voids content at higher gyration levels. The P_{ba} parameter demonstrated that Kraft lignin has a dual role in the asphalt mix, acting as both a binder replacement and a filler.

The determination of optimal construction temperatures for the various mixes highlighted the ability of Sasobit to effectively reduce the construction temperatures of lignin-modified mixes. The combined use of Kraft lignin and Sasobit in the WMA-20L3S mix allowed for the successful mitigation of the increased temperatures caused by Kraft lignin, resulting in construction temperatures identical to the HMA-REF mix.

From a sustainability perspective, both materials demonstrated their potential to reduce bitumen content. The reduction in bitumen content, particularly in the WMA-20L3S mix, highlights the resource-saving benefits of these materials. Kraft lignin, as a renewable material, offers an eco-friendly alternative to petroleum-based binders, while Sasobit enhances the energy efficiency of the construction process by lowering production temperatures.

The volumetric and mass analyses showed that the WMA-20L3S mix closely mirrored the reference mix, maintaining consistent performance despite the addition of Kraft lignin and Sasobit. Kraft lignin role as a partial filler reduced binder absorption.

Finally, the addition of 20 % Kraft lignin and 3 % Sasobit proved to be a viable strategy for producing sustainable asphalt mixtures. The WMA-20L3S mix, in particular, exhibited performance characteristics closely aligned with the reference mix, making it a promising candidate for environmentally friendly pavement solutions. Further research is recommended to explore the mechanical performance of these modified asphalt mixtures.

7.7 Further Developments

While this study provides valuable insights into the effects of Kraft lignin and Sasobit on asphalt mixtures, there are several areas for further development to enhance the understanding and application of these materials in sustainable pavement solutions.

1. Comprehensive mechanical performance testing: In addition to the findings from this study, future research should include a comprehensive evaluation of the mechanical performance of asphalt mixtures containing Kraft lignin and Sasobit. This should cover key aspects such as water susceptibility, low-temperature cracking resistance, fatigue performance, and rutting resistance to ensure these mixtures perform well under diverse environmental and loading conditions.

2. Long-term field performance: Although the laboratory results demonstrate the potential benefits of incorporating Kraft lignin and Sasobit into asphalt mixtures, it is essential to evaluate their long-term performance under real-world conditions.

3. Investigation of alternative additives and materials: The combination of Kraft lignin and Sasobit proved effective in mitigating some of the negative effects of increased construction temperatures associated with Kraft lignin. However, further research into other potential bio-based or chemical materials could yield additional ways to optimize the mixture for improved performance and sustainability.

4. Life cycle assessment (LCA): A comprehensive LCA should be conducted to quantify the environmental benefits of using Kraft lignin and Sasobit in asphalt mixtures.

5. Industrial scale-up: The economic viability of Kraft lignin is still a subject of research, particularly due to its current high production costs. Further research into large-scale production methods and industrial applications of Kraft lignin in asphalt would be beneficial.

6. Binder-additive interaction studies: Investigating the chemical and mechanical interactions between Kraft lignin, Sasobit, and bitumen on a molecular level could yield deeper insights into how these materials impact the binder's properties.

By addressing these areas of further development, the asphalt industry can continue to move towards more sustainable and efficient pavement solutions, reducing the environmental footprint of road construction while maintaining high performance standards.

CHAPTER 8

COMPREHENSIVE SYNTHESIS OF EXPERIMENTAL FINDINGS AND GENERAL DISCUSSION

8.1 Introduction

Sustainable practices in asphalt production have become a key focus in mitigating the environmental challenges posed by conventional methods. Traditional asphalt production relies heavily on oil-based bitumen and high-temperature processes, leading to significant energy consumption and greenhouse gas emissions. To reduce these impacts and improve the performance of asphalt pavements, sustainable additives—particularly bio-based materials and Warm Mix Asphalt (WMA) technologies—have gained increasing attention as viable alternatives. Among these, Kraft lignin and Sasobit exhibit significant potential to enhance the sustainability and performance of bitumen and asphalt mixtures.

The research presented in this PhD thesis investigated the potential of these sustainable additives—Kraft lignin and Sasobit—for enhancing both the environmental and performance characteristics of bitumen and asphalt mixtures. The study was structured into an initial experiment and three well-defined phases, each addressing distinct but interconnected research objectives. Each phase provided critical insights into the behavior of these additives under varying conditions, including their individual and combined effects on bitumen properties, blending protocols, and the feasibility of their application in both Hot Mix Asphalt (HMA) and Warm Mix Asphalt (WMA).

While each phase yielded valuable independent findings, it is essential to integrate and synthesize these results to present a cohesive understanding of their broader impact on sustainable asphalt technologies. This chapter provides a comprehensive synthesis of the research outcomes, linking the different experimental phases and their findings into a cohesive narrative.

8.2 Summary of Research Objectives

The primary objective of this PhD research was to investigate the potential of Kraft lignin as a sustainable additive in asphalt industry while ensuring performance improvements. The research was structured into an initial experiment followed by three systematic phases, each designed to evaluate the effects of Kraft lignin and Sasobit on bitumen and asphalt mixtures. To provide a clear and structured overview of the research conducted in this thesis, Table 8.1 presents the experimental framework and scope of study. Each phase systematically investigated the influence of Kraft lignin and Sasobit on bitumen and asphalt properties.

1. Initial experiment: Investigation of Particle Size Distribution of Different Lignin Types
    - Characterize the particle size distribution (PSD) of various lignin types.
    - Examine the influence of processing methods of lignin on PSD.
2. Phase 1: Influence of Blending Conditions on Chemo-Thermal Characteristics of Lignin-Modified Bitumen
    - Determine optimal blending conditions (High-Shear Mixer vs. Mechanical Mixer) for Kraft lignin incorporation into bitumen.
    - Evaluate the impact of Kraft lignin on viscosity and viscoelastic behavior.
    - Assess thermal behavior, chemical interactions between Kraft lignin and bitumen, and morphology of the Kraft lignin and lignin-modified bitumen samples.
3. Phase 2: Synergistic Effects of Sasobit and Kraft lignin on Bitumen Properties
    - Investigate how Sasobit mitigates viscosity increase in lignin-modified bitumen.
    - Evaluate the rheological properties including deformation resistance, and low-temperature performance.
    - Analyze the combined effects of lignin and Sasobit on chemo-thermal properties.
4. Phase 3: Evaluating the Effect of Kraft Lignin and Sasobit on Asphalt Mix Properties and Construction Temperatures
    - Examine how lignin and Sasobit influence asphalt mix volumetric and mass properties.
    - Determine their impact on construction temperatures and compaction behavior.
    - Assess the feasibility of incorporating these additives into practical asphalt production.

Table 8.1 provides a structured summary of research phases, sample details, and testing methods, illustrating the experimental approach, materials used, and key variables analyzed in each phase.

Table 8.1 Overview of research phases, sample details, and testing methods

Research Phases	Initial	1st Phase	2nd Phase	3rd Phase
Research Area	Lignin	BITUMEN	BITUMEN	ASPHALT MIX
Samples	Different types of lignin	5, 10, 20% Kraft lignin	5, 10, 20% Kraft lignin	20% Kraft lignin
		MM, HSM	1, 3% Sasobit	3% Sasobit
Number of Samples	16 Lignin samples	9 Samples: VB, VB-MM, VB-HSM, 5L-MM, 5L-HSM, 10L-MM, 10L-HSM, 20L-MM, 20L-HSM	13 Samples: VB, VBM, 1S, 3S, 5L, 5L1S, 5L3S, 10L, 10L1S, 10L3S, 20L, 20L1S, 20L3S	4 Samples: HMA-REF, HMA-20L, WMA-3S, WMA-20L3S
Tests	Laser Granulometry (PSD)	PSD (Kraft lignin), BRV, DSR, FTIR, ESEM, TGA, DSC	FTIR, TGA, BRV, DSR, MSCR, BBR	G_{mm}, SGC, Compactability, Volumetric and Mass Properties, Construction Temperatures

8.3 Key Research Findings and Technical Insights

8.3.1 Effect of Lignin Source and Processing Methods on Its Properties

The findings from the initial experiment demonstrated that all types of lignin are not a uniform or standardized material that can be effectively used as an asphalt additive, extender, or replacer without considering its source, chemical properties, and processing methods. The findings from the PSD analysis revealed that lignin derived from different plant sources and subjected to various processing techniques exhibits distinct physical and chemical characteristics, which can potentially influence its performance in asphalt modification. Variability in plant origin affects the inherent chemical composition of lignin, while processing methods such as grinding and modification, further alter its granulometric properties and dispersion behavior. Even the color of lignin powder varies significantly across different sources, indicating inherent differences in composition. The study revealed that grinding and modification processes do not always result in finer and more uniform particles; instead, some samples exhibited particle agglomeration or broader size distributions, highlighting the significance of processing methods. These findings underscore the complexity and heterogeneity of lignin, emphasizing that its potential for asphalt modification cannot be generalized. Instead, a case-specific evaluation of each lignin type is essential to determine its compatibility with bitumen and its functional role in asphalt mixtures. While the PSD analysis provided crucial insights into lignin’s variability, further experimental research is required.

8.3.2 Influence of Kraft Lignin on Bitumen Properties

The findings from the first phase demonstrated that the blending process plays a crucial role in ensuring the successful incorporation of Kraft lignin into bitumen using the wet process. The results confirmed that blending speed significantly impacts the final properties of lignin-modified bitumen, making it essential to optimize mixing conditions. In particular, high-shear mixer (HSM) was shown to be more effective than mechanical mixer (MM), as it facilitated better dispersion of lignin particles within the bitumen matrix, leading to a more uniform and stable modified bitumen.

The study further highlighted that the addition of Kraft lignin generally increases the viscosity, stiffness, high-temperature stability, and $|G|^*/\sin(\delta)$ value of bitumen. This indicates that lignin acts as a reinforcement agent, enhancing the binder’s resistance to deformation at elevated temperatures. However, the results also revealed that the addition of Kraft lignin reduces the thermal stability of bitumen, suggesting that lignin-modified binders may be more susceptible to degradation under prolonged thermal exposure.

Despite these changes in physical properties, chemical analysis confirmed that Kraft lignin does not chemically react with bitumen but rather alters its structure through physical interactions. Microscopic analysis further demonstrated that as the lignin content increased, its distribution within the fibril structure of bitumen became more widespread, without significant particle aggregation. This suggests that lignin can be successfully integrated into bitumen at contents up to 20% without major phase separation issues.

Overall, these findings emphasize that the effectiveness of Kraft lignin as a bitumen modifier is highly dependent on blending conditions. Proper selection of mixing speed and methodology is essential to achieving a homogeneous and stable modified binder. While Kraft lignin enhances the high-temperature performance of bitumen, its impact on viscosity and thermal stability must be carefully managed to ensure practical applicability in asphalt production.

8.3.3 Synergistic Effects of Kraft lignin and Sasobit on Bitumen Performance

The findings from the second phase demonstrated that the combined use of Kraft lignin and Sasobit significantly influences the chemo-thermal and rheological properties of bitumen, presenting both advantages and challenges. The study systematically evaluated the interactions between these two additives and their effects on viscosity, thermal stability, and mechanical performance at both high and low temperatures.

One of the key observations was that Kraft lignin and Sasobit interact primarily through physical mechanisms rather than chemical modifications, as confirmed by FTIR analysis. This suggests that their effects on bitumen properties are governed by their dispersion and distribution rather than the formation of new chemical bonds within the binder. Thermal analysis (TGA) revealed that increasing Kraft lignin content reduces the thermal stability of bitumen, whereas Sasobit at lower concentrations slightly improves stability, but higher concentrations offer no additional benefit. Furthermore, within the operational temperature range of asphalt production (< 200 °C), lignin-modified bitumen exhibited a higher degradation rate, while Sasobit had a negligible influence in this temperature range.

A critical issue associated with Kraft lignin modification is the substantial increase in viscosity, which can present challenges for mixing, pumping, and compaction. However, Sasobit effectively counteracts this effect, reducing viscosity and improving workability. The optimal balance was identified in the 5L3S formulation (5% Kraft lignin and 3% Sasobit), where the modified bitumen achieved viscosity levels comparable to virgin bitumen.

Rheological testing confirmed that both additives enhance bitumen’s high-temperature resistance and rutting resistance. However, despite these high-temperature advantages, the modified bitumen exhibited increased stiffness and brittleness, leading to a decline in low-temperature performance.

These findings underscore the potential of Sasobit to mitigate some of the adverse effects of Kraft lignin on bitumen, particularly in terms of viscosity. However, the study highlights that while the combination of these two additives enhances mechanical performance at high temperatures, it compromises resistance to thermal cracking at low temperatures. This trade-off must be carefully managed to ensure balanced performance across different climatic conditions.

8.3.4 Influence of Kraft Lignin and Sasobit on Asphalt Mix properties

The findings from the third phase demonstrated that the incorporation of Kraft lignin and Sasobit into asphalt mixtures significantly affects compaction behavior, construction temperatures, and volumetric and mass properties, offering both challenges and opportunities for sustainable pavement solutions. The study systematically examined the interactions of these additives, providing key insights into their effects on asphalt mix design and performance.

A critical observation was that Kraft lignin reduces the compactability of asphalt mixtures, as evidenced by the higher air voids content. The volumetric analysis also revealed that Kraft lignin plays a dual role, acting both as a binder replacement and a filler. This characteristic led to increased air voids and binder absorption, reinforcing the necessity of optimizing its dosage and integration method to achieve desirable mix properties.

The study further highlighted the role of Sasobit in mitigating the temperature-related challenges associated with Kraft lignin. The determination of construction temperatures demonstrated that Sasobit effectively reduces the elevated temperatures required for lignin-modified asphalt. This combination successfully lowered production and compaction temperatures to levels comparable to conventional hot mix asphalt, improving the energy efficiency and environmental sustainability of the asphalt production process.

From a sustainability standpoint, the co-incorporation of Kraft lignin and Sasobit contributes to reducing bitumen content without compromising performance. The mix with both Kraft lignin and Sasobit maintained volumetric and mass properties closely aligned with the reference mix, demonstrating that these bio-based and viscosity-reducing additives can be integrated into asphalt formulations without adversely affecting structural integrity. Overall, the combined use of 20% Kraft lignin and 3% Sasobit proved to be a viable approach for producing sustainable asphalt mixtures.

8.4 Key Contributions to Sustainable Asphalt Engineering

This research makes significant contributions to the advancement of sustainable asphalt technology, providing critical insights into the integration of Kraft lignin in bitumen and asphalt mixtures. The findings offer a deeper understanding of how Kraft lignin and Sasobit additives interact, addressing key challenges related to their application while identifying opportunities to enhance environmental and performance benefits. The major contributions of this study are summarized as follows:

- **Lignin Types Vary Significantly Based on Source and Processing:** Lignin is not a single, uniform material, but rather a diverse class of biopolymers with varying chemical and physical properties depending on its source, and processing conditions.
- **Effective Blending of Kraft Lignin Requires High-Shear Mixing:** The incorporation of Kraft lignin into bitumen requires careful attention to blending conditions, as

improper mixing can significantly affect the final binder properties. High-shear mixing (HSM) proved to be more effective than mechanical mixing (MM), ensuring better dispersion, improved viscosity control, and more uniform modification. The findings highlight that mixing rate and method are critical factors in achieving a consistent and high-quality lignin-modified bitumen, reinforcing the importance of selecting an appropriate blending approach for optimal performance.

- **Sasobit Mitigates the High Viscosity of Lignin-Modified Bitumen:** The findings demonstrated that Sasobit plays a crucial role in counteracting the viscosity increase caused by Kraft lignin in bitumen modification. These insights highlight the potential of combining bio-based and viscosity-reducing additives to enhance the feasibility of lignin-modified asphalt production.
- **Balancing Compactability and Volumetric Properties in Lignin-Modified Asphalt Mixes with Sasobit:** The findings demonstrated that Kraft lignin influences compactability, binder absorption, and volumetric properties in asphalt mixtures. While lignin increases air void content and binder absorption, Sasobit effectively counteracts these effects by enhancing compaction and reducing construction temperatures.
- **Advancing Sustainable Asphalt Production with Kraft Lignin:** This research demonstrated that incorporating 20 % Kraft lignin and 3 % Sasobit enables the production of asphalt mixes with volumetric properties comparable to conventional Hot Mix Asphalt (HMA) while significantly optimizing construction temperatures.
- **Advancing the Adoption of Bio-Based Additives in Pavement Engineering:** This research supports the circular economy by promoting the use of lignin, a renewable byproduct, as a partial replacer to petroleum-based binders.

This chapter has provided a comprehensive synthesis of the research findings, linking the key outcomes of each phase into a unified framework. The study has demonstrated that integrating Kraft lignin and Sasobit into bitumen and asphalt mixtures, addressing key technical challenges and reinforcing their potential for large-scale implementation in sustainable pavement engineering.

CONCLUSION

The transition toward sustainable infrastructure necessitates innovations in asphalt technology to minimize environmental impact while maintaining performance standards. This research investigated the potential of Kraft lignin as sustainable additive in bitumen and asphalt mixtures, focusing on its influence on blending, rheological and chemo-thermal properties, compaction behavior, and construction temperatures. The findings demonstrated that Kraft lignin is a highly variable material whose properties depend on its source, chemical characteristics, and processing methods. Additionally, the study confirmed that incorporating lignin into bitumen requires careful blending techniques, with high-shear mixing proving more effective than mechanical mixing in ensuring uniformity and stability. The results further highlighted the dual role of lignin in asphalt mixtures, acting as both a partial binder replacement and a filler, influencing viscosity, air void content, and compaction behavior.

The integration of Sasobit alongside Kraft lignin offered a practical solution to mitigate the viscosity challenges associated with lignin-modified bitumen, improving workability and lowering construction temperatures. The synergy between these two additives enabled the formulation of asphalt mixtures with characteristics comparable to conventional hot mix asphalt (HMA), while contributing to energy efficiency and resource conservation. Despite these advantages, the study also revealed certain trade-offs, particularly at low temperatures, where increased stiffness and brittleness could affect long-term durability. These findings emphasize the need for a balanced approach when incorporating bio-based additives, ensuring that improvements in high-temperature stability do not come at the expense of flexibility and resistance to thermal cracking.

This research contributes to the ongoing efforts in developing environmentally friendly asphalt technologies, demonstrating that bio-based additives such as Kraft lignin can serve as viable partial alternatives to petroleum-based binders. The findings provide a foundation for further exploration into optimizing lignin-modified asphalt formulations through advanced mix designs, long-term durability assessments, and large-scale field applications. While the laboratory results are promising, future research should focus on addressing performance variability across different lignin sources, evaluating the mechanical durability of modified asphalt, and validating these findings under real-world conditions. By advancing the use of renewable materials in pavement engineering, this study supports the broader transition toward sustainable and energy-efficient road infrastructure.

RECOMMENDATIONS

This research provides a strong foundation for incorporating Kraft lignin and Sasobit into bitumen and asphalt mixtures to promote sustainability in the asphalt industry. However, further investigations and developments are essential to fully understand and optimize their potential. The following recommendations outline key areas for future research and practical advancements:

1) **Advanced Analytical Techniques:** Employ advanced methods such as TGA-FTIR to gain a deeper understanding of the chemical changes occurring during the thermal degradation of lignin-modified bitumen. Utilize FTIR to determine carbonyl and sulfoxide indices and analyze the kinematic effects of lignin-modified bitumen through TGA for a more detailed assessment of its chemical and thermal behavior.
2) **Comprehensive Mechanical Performance Evaluation:** Future studies should assess key mechanical properties, including water susceptibility, fatigue resistance, rutting resistance, and low-temperature cracking performance, to ensure the long-term durability of asphalt mixtures containing Kraft lignin and Sasobit.
3) **Life Cycle Assessment (LCA):** Conduct detailed LCAs to quantify the environmental impact of incorporating Kraft lignin and Sasobit into asphalt production. These assessments should include comparisons to conventional mixtures and consider the entire lifecycle from material sourcing to end-of-life scenarios.
4) **Long-Term Field Performance:** Extend research to include long-term field studies under real-world traffic and environmental conditions. These evaluations will provide critical insights into the durability and reliability of these modified mixtures over time.
5) **Economic Feasibility and Industrial Scale-Up:** Investigate the economic viability of large-scale production and application of Kraft lignin and Sasobit in asphalt mixtures. This includes exploring cost-effective production methods and supply chain strategies for these materials.

6) **Binder-Additive Interaction Studies:** Investigate the chemical and mechanical interactions between Kraft lignin, Sasobit, and bitumen on a molecular level. These studies can yield valuable insights into optimizing blending protocols and improving material performance.
7) **Investigation of Alternative Additives:** Research other bio-based or chemical additives that could complement or enhance the effects of Kraft lignin and Sasobit, further improving the sustainability and performance of asphalt mixtures.
8) **Application of Warm Mix Asphalt (WMA):** Extend laboratory studies to investigate the use of Kraft lignin and Sasobit in different method of WMA, focusing on reducing energy consumption and emissions during production while maintaining or improving mechanical performance.
9) **Integration into Diverse Asphalt Applications:** Study the feasibility and performance of these additives across a broader range of asphalt applications, including modified and unmodified bitumens, and cold mix asphalts.
10) **Broader Sustainability Considerations:** Explore strategies to further reduce the environmental footprint of asphalt production by integrating renewable materials such as Kraft lignin with innovative technologies for greener pavement solutions.

By addressing these areas, the asphalt industry can advance toward more sustainable, efficient, and high-performing pavement technologies.

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