

EFFECT OF BINDER SOURCES ON THE CHEMICAL AND RHEOLOGICAL
PROPERTIES OF WARM MIX ASPHALT BINDERS

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SEMİHA UHDE YILDIRIM

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submitted by **SEMİHA UHDE YILDIRIM** in partial fulfillment of the requirements for the degree of **Master of Science in Civil Engineering, Middle East Technical University** by,

Prof. Dr. Halil Kalıpçılar
Dean, **Graduate School of Natural and Applied Sciences**

Prof. Dr. Erdem Canbay
Head of the Department, **Civil Engineering**

Assoc. Prof. Dr. Hande Işık Öztürk
Supervisor, **Civil Engineering, METU**

Prof. Dr. Murat Güler
Co-Supervisor, **Civil Engineering, METU**

Examining Committee Members:

Prof. Dr. İsmail Özgür Yaman
Civil Engineering, METU

Assoc. Prof. Dr. Hande Işık Öztürk
Civil Engineering, METU

Prof. Dr. Murat Güler
Civil Engineering, METU

Prof. Dr. Cihangir Tanyeli
Chemistry, METU

Prof. Dr. Mustafa Şahmaran
Civil Engineering, Hacettepe University

Date: 24.01.2024

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name Last name : S. Uhde Yıldırım

Signature :

ABSTRACT

EFFECT OF BINDER SOURCES ON THE CHEMICAL AND RHEOLOGICAL PROPERTIES OF WARM MIX ASPHALT BINDERS

Yıldırım, S. Uhde
Master of Science, Civil Engineering
Supervisor: Assoc. Prof. Dr. Hande Işık Öztürk
Co-Supervisor: Prof. Dr. Murat Güler

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The chemical properties of bituminous binders, which vary based on the source, influence their physical and rheological characteristics. Due to the advancements in the additive industry, studies in recent years have been focusing not only on physical and rheological properties but also on chemical properties. Therefore, this study initially examined these properties of binders obtained from the Batman refinery, a domestic binder source, and the Kırıkkale refinery, an imported binder source, at two different penetration grades (50/70 and 70/100). Chemical properties are analyzed using the weight-base SARA (Saturate, Aromatic, Resin, and Asphaltene) and Fourier Transform Infrared Spectrometry (FTIR). The relation between the chemical, physical, and rheological characteristics was analyzed by considering the binder source. Moreover, 50/70 penetration grade binders from two different refineries are modified with two Warm Mix Asphalt (WMA) additives. Although it is known that the chemical properties of bituminous binders are changed with WMA additives, the effect has not been quantified in earlier studies. This thesis addresses the lack of understanding between the chemical, physical, and rheological properties of WMA-modified binders. The findings indicate that the binder source dominates the relationships and behaviors when modified with WMA additives. Thus, it is not

sufficient to only consider the rheological properties of bituminous binders but also the chemical properties should be investigated. A linear relationship between the Gaestel indices of binders and the Aging index is determined for both unmodified and modified binders. It indicates that the weight-based SARA and FTIR analysis correlate well.

Keywords: SARA, FTIR, Warm Mix Asphalt (WMA), Gaestel Index, Aging Index

ÖZ

BAĞLAYICI KAYNAKLARININ ILIK KARIŞIM ASFALTIN (IKA) KİMYASAL VE REOLOJİK ÖZELLİKLERİNE ETKİSİ

Yıldırım, S. Uhde
Yüksek Lisans, İnşaat Mühendisliği
Tez Yöneticisi: Doç. Dr. Hande Işık Öztürk
Ortak Tez Yöneticisi: Prof. Dr. Murat Güler

Ocak 2024, 175 sayfa

Bitümlü bağlayıcıların kimyasal özellikleri, kaynağa bağlı olarak değişir ve fiziksel ile reolojik özelliklerini etkiler. Katkı endüstrisindeki ilerlemeler nedeniyle, son yıllarda yapılan çalışmalar sadece fiziksel ve reolojik özelliklere odaklanmakla kalmayıp aynı zamanda kimyasal özelliklere de odaklanmaktadır. Bu nedenle, bu çalışmada başlangıçta, yerli bir bağlayıcı kaynağı olan Batman rafinerisinden ve ithal bir bağlayıcı kaynağı olan Kırıkkale rafinerisinden elde edilen bağlayıcıların bu özelliklerini iki farklı penetrasyon sınıfında (50/70 ve 70/100) incelendi. Kimyasal özellikler, ağırlık bazlı DARA (Doymuş, Aromatik, Reçine, and Asfalt) ve Fourier Transform Infrared Spectrometry (FTIR) kullanılarak analiz edilmiştir. Kimyasal, fiziksel ve reolojik özellikler arasındaki ilişki bağlayıcı kaynağı göz önüne alınarak analiz edilmiştir. Ayrıca, iki farklı rafineriden elde edilen 50/70 penetrasyon sınıfındaki bağlayıcılar, iki farklı Ilık Karışım Asfalt (IKA) katkısı ile modifiye edilmiştir. Bitümlü bağlayıcıların kimyasal özelliklerinin IKA katkıları ile değiştiği bilinmesine rağmen, bu etki daha önceki çalışmalarda nicelendirilmemiştir. Bu tez, IKA ile modifiye edilmiş bağlayıcıların kimyasal, fiziksel ve reolojik özellikleri arasındaki anlayış eksikliğine odaklanmaktadır. Bulgular, bağlayıcı kaynağının IKA

katkıları ile modifiye edildiğinde ilişkileri ve davranışları domine ettiğini göstermektedir. Bu nedenle, bitümlü bağlayıcıların sadece reolojik özelliklerini incelemek yeterli değildir, aynı zamanda kimyasal özelliklerini de incelemek gerekmektedir. Bağlayıcıların Gaestel indeksleri ile Aging indeksi arasında hem modifiye edilmemiş hem de modifiye edilmiş bağlayıcılar için lineer bir ilişki belirlenmiştir. Bu durum, ağırlık bazlı DARA ve FTIR analizinin iyi bir şekilde korele olduğunu göstermektedir.

Anahtar Kelimeler: DARA, FTIR, Ilık Karışım Asfalt (IKA), Gaestel indeksi, Yaşlanma indeksi

To my lovely grandmother, Semiha Göl

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TABLE OF CONTENTS

ABSTRACT.....	v
ÖZ.....	vii
ACKNOWLEDGMENTS.....	x
TABLE OF CONTENTS.....	xi
LIST OF TABLES.....	xiv
LIST OF FIGURES.....	xvi
LIST OF ABBREVIATIONS.....	xix
CHAPTERS	
1 INTRODUCTION.....	1
1.1 Research Objective.....	1
1.2 Motivation and Steps of the Study.....	4
1.3 Outline of the Research.....	5
2 LITERATURE REVIEW.....	7
2.1 Separation of Chemical Fraction of Bituminous Binders.....	7
2.2 Methods for Separating Bituminous Binders into Polar Fractions.....	10
2.2.1 Separation Process of Asphaltenes and Maltenes.....	10
2.2.2 Separation process of maltene into saturate, aromatic, and resin.....	15
2.3 Solubility Parameters of the Bituminous Binder.....	25
2.4 The Relationship Between SARA Fractions and Physical Properties of Bituminous Binders.....	28

2.5	Aging Effect on SARA Fractions	29
2.6	The Relationship Between SARA Fractions and Rheological Properties of Bituminous Binders	31
2.7	Warm Mix Asphalt (WMA) Additives	33
2.7.1	Effect of Sasobit Additive to the Bituminous Binder Properties	35
2.7.2	Comparison of Sasobit and Evotherm Additive	37
2.8	Fourier Transform Infrared Spectroscopy (FTIR)	39
3	MATERIALS AND METHODS	41
3.1	Materials	42
3.2	Preparation of Modified Binders with WMA additives.....	45
3.3	Bituminous Binders Physical Characteristics	46
3.4	Rheological Properties of Bituminous Binders	49
3.5	Experimental Study of weight-based SARA Simplified Technique	53
3.5.1	Details of Test Setup	53
3.5.2	Details of the Solvents.....	54
3.5.3	Preparation Stage of Bituminous Binder.....	55
3.5.4	Separation of Bituminous Binder into Two Fractions: Asphaltene and Maltene	56
3.5.5	Drying Process of Asphaltenes and Maltenes	58
3.5.6	Separation of Maltene into Three Fractions: Saturate, Aromatic and Resin	60
3.5.7	Calculation of SARA Fractions.....	65
3.5.8	Gaestel Index (Ic)	66
3.6	Fourier Transform Infrared Spectroscopy (FTIR)	67
4	DISCUSSION AND RESULTS.....	71

4.1	Unmodified Bituminous Binders.....	71
4.1.1	Physical Properties of Unmodified Bituminous Binders.....	71
4.1.2	Relationship Between SARA Fractions and Physical Properties	71
4.1.3	Rheological Properties of Unmodified Bituminous Binders	75
4.1.4	Relationship Between SARA Fractions and Rheological Properties	83
4.1.5	Gaestel Index of Unmodified Bituminous Binders.....	90
4.1.6	FTIR Analysis Results of Unmodified Bituminous Binders	92
4.2	Modified Bituminous Binders.....	101
4.2.1	Physical Properties of Modified Bituminous Binders	101
4.2.2	Relationship Between SARA Fractions and Physical Properties ...	103
4.2.3	Rheological Properties of Bituminous Binder with WMA Additive 108	
4.2.4	Relationship Between Rheological Properties and SARA Fractions of Modified Bituminous Binders.....	119
4.2.5	Gaestel Index (Ic) of Modified Bituminous Binders	128
4.2.6	FTIR Analysis Results of Modified Bituminous Binders.....	131
5	CONCLUSION	139
5.1	Major Findings in This Study.....	139
5.2	Recommendations	143
	REFERENCES	145
A.	Rheological Data	163
B.	FTIR Graphs.....	167

LIST OF TABLES

TABLES

Table 2.1 Summary of the separation methods of asphaltene fraction.....	14
Table 2.2 HSP of the Asphaltene and Maltene Fraction (Li et. al., 2022)	27
Table 2.3 RED values of SARA Fractions (Park et al. al., 2022)	28
Table 3.1 Bituminous binder standard (KGM, 2013).....	47
Table 3.2 Physical properties of base bituminous binders	47
Table 3.3 The physical properties of modified bituminous binders obtained from Kırıkkale refinery	48
Table 3.4 The physical properties of modified bituminous binders obtained from Batman refinery	48
Table 3.5 Mass loss of base and modified binders	50
Table 3.6 Solvents used for separation of maltene into S-A-R fractions	55
Table 4.1 Performance Grade (PG) of unmodified bituminous binders	77
Table 4.2 Unaged bituminous binders DSR results between 58-76°C at 10 Hz	78
Table 4.3 Relationship between Gaestel Index and AI_{FTIR}	99
Table 4.4 True and performance grade (PG) of modified bituminous binders	109
Table 4.5 Rheological properties of unaged modified bituminous binders.....	111
Table 4.6 Rheological properties of short-term aged modified bituminous binders	112
Table 4.7 Rheological properties of long-term aged modified bituminous binders	114
Table 4.8 Asphaltene content and true grade of modified binders from Kırıkkale refinery	125
Table 4.9 Asphaltene content and true grade of modified binders from Batman refinery	125
Table 4.10 High-Temperature Properties of Modified Binders Obtained Kırıkkale Refinery	126

Table 4.11 High-Temperature Properties of Modified Binders Obtained from Batman Refinery	127
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LIST OF FIGURES

FIGURES

Figure 3.1. Flow diagram of the experimental program.....	42
Figure 3.2. Bituminous binders used in this study	44
Figure 3.3. The Stirring process of bituminous binder and n-heptane	56
Figure 3.4. a) Asphaltene-Maltene separation b) Maltene-n-heptane solutions.....	58
Figure 3.5. Dried maltene vials	59
Figure 3.6. Clean and used PTFE filters.....	60
Figure 3.7. Process of pre-washing of SPE cartridge with 20 ml n-heptane.....	61
Figure 3.8. 15 ml Maltene solution poured into SPE cartridge b)10 ml n-heptane added after Maltene separation for cleaning	62
Figure 3.9. Toluene: n-heptane poured into SPE cartridge	63
Figure 3.10. DCM: Methanol poured into SPE cartridge.....	64
Figure 3.11. S-A-R fractions	65
Figure 3.12. a) Saturate fraction before and after drying b) Aromatic fraction before and after drying c) Resin fraction before and after drying	65
Figure 3.13. ATR-FTIR Analysis instrument.....	69
Figure 4.1. SARA fractions of unaged bituminous binders	74
Figure 4.2. Viscosity results of unmodified bituminous binders.....	75
Figure 4.3. Master curves of bituminous binders exposed to aging (Complex shear modulus vs. Frequency).....	80
Figure 4.4. Master curves of bituminous binders exposed to aging (Phase angle vs. Frequency).....	82
Figure 4.5. The change in SARA fractions of KK50/70 with short-term and long-term aging.....	85
Figure 4.6. The change in SARA fractions of BM50/70 with short-term and long-term aging.....	85
Figure 4.7. The change in SARA fractions of KK70/100 with short-term and long-term aging.....	87

Figure 4.8. The change in SARA fractions of KK70/100 with short-term and long-term aging	87
Figure 4.9. Gaestel Index of unmodified bituminous binders	90
Figure 4.10. Change of Gaestel Index with aging	92
Figure 4.11. FTIR Spectra of unmodified bituminous binder.....	93
Figure 4.12. Change of the carbonyl and sulfoxide indices of bituminous binder due to aging (Kırıkkale refinery)	94
Figure 4.13. Change of the carbonyl and sulfoxide indices of bituminous binder due to aging (Batman refinery).....	95
Figure 4.14. Aging Indices of unmodified bituminous binders	97
Figure 4.15. Aging Indices of bituminous binder obtained from Kırıkkale refinery	98
Figure 4.16. Aging Indices of bituminous binder obtained from Batman refinery	98
Figure 4.17. Gaestel Index and Aging Index of unmodified bituminous binders...	99
Figure 4.18. The effect of WMA additives on the viscosity of bituminous binders (Kırıkkale Refinery).....	102
Figure 4.19. The effect of WMA additives on the viscosity of bituminous binders (Batman Refinery)	103
Figure 4.20. The effect of WMA additives on SARA fractions (Kırıkkale Refinery)	106
Figure 4.21. The effect of WMA additives on SARA fractions (Batman Refinery)	106
Figure 4.22. Viscosity and temperature graph of modified bituminous binders...	108
Figure 4.23. Complex shear modulus vs frequency master curve of modified bituminous binders.....	117
Figure 4.24. Phase angle vs frequency master curve of modified bituminous binders	119
Figure 4.25. The change in SARA fractions of modified KK50/70 binder after Short-Term Aging.....	121

Figure 4.26. The change in SARA fractions of modified BM50/70 binder after Short-Term Aging	122
Figure 4.27. The changes in SARA fractions of modified KK50/70 binder after long-term aging	123
Figure 4.28. The change in SARA fractions of modified BM50/70 binder after long-term aging	124
Figure 4.29. Gaestel Index of Unmodified and Modified Bituminous Binders	129
Figure 4.30. Gaestel Indices of modified and aged KK50/70 binder	130
Figure 4.31. Gaestel Indices of modified and aged BM50/70 binder	131
Figure 4.32. FTIR spectra of modified bituminous binder obtained from Kırıkkale refinery	132
Figure 4.33. FTIR spectra of modified bituminous binder obtained from Batman refinery	133
Figure 4.34. Change of the carbonyl and sulfoxide indices of modified bituminous binder (Kırıkkale Refinery)	134
Figure 4.35. Change of the carbonyl and sulfoxide indices of modified bituminous binder (Batman Refinery).....	135
Figure 4.36. Aging indices of modified bituminous binders obtained from Kırıkkale refinery	136
Figure 4.37. Aging indices of modified bituminous binders obtained from Batman refinery	137
Figure 4.38. Gaestel and aging indices of modified bituminous binders	138

LIST OF ABBREVIATIONS

ABBREVIATIONS

AASHTO : The American Association of State Highway and Transportation

AD : Asphaltene Determination

ASTM : American Society for Testing and Materials

DSR : Dynamic Shear Rheometer

ELSD: Evaporative Light Scattering Detector

FTIR : Fourier Transform Infrared Spectrometry

HMA : Hot Mix Asphalt

HPLC : High Pressure Liquid Chromatography

HSP : Hansen Solubility Parameter

PAV : Pressure Aging Vessel

PTFE : Polytetrafluoroethylene

RED : Relative Energy Difference

RTFO : Rolling Film Thin Oven

SARA : Saturate, Aromatic, Resin, Asphaltene

TLC-FID : Thin Layer Chromatography Flame Ionization Detection

WMA : Warm Mix Asphalt

CHAPTER 1

INTRODUCTION

1.1 Research Objective

The bituminous binders are characterized by their physical and rheological properties. However, it is crucial to acknowledge that the chemical characteristics of bituminous binders affect their physical and rheological properties (Sultana & Bhasin, 2014; Zenke, 1977; Weigel & Stephan, 2018). Therefore, chemical properties are as important as physical and rheological properties in understanding and characterizing bituminous binders.

Bituminous binders have a complex chemical structure due to the presence of a wide variety of molecules. Although bituminous binders are typically composed of carbon and hydrogen, they also contain 5-10% heteroatoms and metals in their structure (Nelson, 1968; Jones, 1992). The presence of heteroatoms and metals in bituminous binders varies depending on the source (Jones, 1992; Redelius, 2015). Consequently, binders from different sources exhibit distinct chemical properties (Corbett, 1969; Michalica et al., 2008; Mirward et al., 2020; Plug et al., 2022). Furthermore, Corbett (1969) revealed that binders with similar physical properties can have different chemical compositions. In summary, the chemical properties of bituminous binders, alongside their physical and rheological characteristics, are significant criteria for characterization.

As aforementioned, understanding the chemical properties of bituminous binders is challenging due to factors such as the complex structure of the binder and the presence of a wide variety of molecular types (Redelius, 2006; Jennings et al., 1992). It has been revealed by many researchers that polar fractions are easier to determine.

Moreover, these studies have already presented the relationship between polarity and asphalt performance (Redelius & Soenen, 2015; Sakib & Bhasin, 2016; Sreeram et al., 2019).

The polar fractions of bituminous binders initially divides into asphaltene and maltene fractions, and the maltene fraction further separates into saturate, aromatic, and resin fractions. These fractions are together named SARA fractions. Asphaltene and resin fractions are black and solid at room temperature, saturates are colorless and liquid at room temperature, and the aromatic fraction is liquid at room temperature, ranging between yellow and red (Corbett, 1969). Upon examining their polarities, it is observed that asphaltene has the highest polarity, followed by resin and aromatic, while saturate exhibits the least polarity (Yarranton & Masliyah, 1996). In the literature, ASTM standards are established for separating bituminous binders into SARA fractions. ASTM D3279: Standard Test Method for n-heptane insoluble and ASTM D6560: Standard Test Method for Determination of Asphaltenes in crude Petroleum and Petroleum products are utilized as methods for separating asphaltene and maltene fractions, employing filtration and reflux. To separate bituminous binders into SARA fractions, ASTM D4124: Standard Test Method for separation of Asphalt into four fractions and ASTM D2007: Standard Test Method for n-Heptane insoluble methods are used. In addition to ASTM methods, other techniques, and analytical methods are also applied for a comprehensive understanding of bituminous binder properties and behaviors. Among these, high-pressure liquid chromatography (HPLC) and thin-layer chromatography flame ionization detection (TLC-FID) are commonly used to separate SARA fractions from the bituminous binder. In the TLC-FID method, it has been reported that a portion of saturate and aromatic fractions is lost. Despite its rapidity, this method exhibits low reproducibility (Fan & Buckley, 2002). Besides, HPLC is a repeatable but considerably expensive method (Ali, 2022). Therefore, a cost-effective, fast, and repeatable technique, the weight-based SARA method, has been developed for separating bituminous binders into SARA fractions by Sakib & Bhasin (2018). Moreover, to gain insights into the chemical characteristics of the

bituminous binder at the molecular level except SARA analysis, various other methods are also used by researchers. Among these methods, Fourier Transform Infrared Spectrometry (FTIR) is generally used to identify the functional groups of the bituminous binder. In this thesis, the chemical properties of the bituminous binder are examined using both the weight-based SARA method and FTIR analysis to have different perspectives.

In Turkey, there are six refineries, five of which distillate imported crude oil, while the Batman refinery only uses domestic crude oil sources. In this study, binders at two penetration grades, 50/70 and 70/100, were obtained from the Kırıkkale refinery, which utilizes imported crude oil, and the Batman refinery, which utilizes domestic crude oil. The physical properties of bituminous binders and their rheological characteristics following short-term and long-term aging processes have been investigated. Additionally, SARA and FTIR analyses have been implemented. The thesis delves into understanding how the characteristics of binders evolve based on their source and explores the impact of their chemical properties on both the physical and rheological properties. The findings of this part of the thesis are intended to provide a basis for the pavement and additive industries.

In line with the evolving road industry, additives in bituminous binders are increasing exponentially due to energy savings, improved workability, and economic benefits. Among these additives, Warm mix asphalt (WMA) additives stand out as they lower mixing and compaction temperatures without compromising asphalt performance. Remarkably, no research currently addresses the chemical properties of bituminous binders modified with Warm Mix Asphalt (WMA) additives concerning the physical and rheological properties. Therefore, this study also examines the chemical, physical, and rheological properties of WMA-modified bituminous binders. For this purpose, two base binders from Kırıkkale and Batman refineries at the same penetration grade (50/70) are modified with two different WMA additives: an organic additive (Sasobit) and a chemical additive (Evotherm). Eventually, this study delves into the chemical properties of bituminous binders modified with WMA additives and investigates how they relate to the physical and

rheological characteristics of the binders. SARA and FTIR analyses are also completed to define the chemical properties of modified bituminous binders. Consequently, this thesis determines the impact of the chemical characteristics of modified and unmodified binders, belonging to two different penetration classes obtained from two binder sources, on their physical and rheological properties.

1.2 Motivation and Steps of the Study

This study aims to contribute valuable insights to the existing literature. Initially, it should be emphasized that there is limited research on the chemical properties of bituminous binders produced in refineries based in Turkey. Through SARA and FTIR analyses, this study reveals the chemical properties of bituminous binders from two different refineries in Turkey. Despite the growing importance of additives in bituminous binders, there is a lack of understanding of the relationship between the chemical, physical, and rheological properties of bituminous binders modified with WMA additives. Moreover, it is unknown how WMA additives affect the chemical structure of bituminous binders, although it is known that the chemical properties of bituminous binders are changed with WMA additives. This study seeks to address these gaps by investigating the influence of the binder's source on the chemical properties of bituminous binders and the extent to which WMA additives affect their chemical properties.

As briefly discussed in the previous section,

The steps of this study are as follows:

- 1- Determining the physical properties of bituminous binders from two different binder sources at two different penetration grades.
- 2- Assessing the rheological properties of the binders by subjecting them to short-term aging (RTFO) and long-term aging (PAV).
- 3- Identifying the chemical properties of unaged, short-term, and long-term aged binders through SARA and FTIR analyses.

- 4- Evaluating the changes in the physical properties of WMA-modified bituminous binders prepared with Sasobit and Evotherm.
- 5- Determining the rheological properties of modified binders through short-term (RTFO) and long-term (PAV) aging processes.
- 6- Establishing the chemical properties of unaged, short-term aged, and long-term aged binders through SARA and FTIR analyses
- 7- Determining the impact of the chemical properties of unmodified and modified bituminous binders from two different sources with two different penetration grades on their physical and rheological properties.

1.3 Outline of the Research

Chapter 2 includes a literature review on the chemical analysis of bituminous binders. This chapter provides detailed discussions on the separation methods of SARA fractions. A summary of the current literature is presented on the relation between SARA fractions and physical and rheological properties of the bituminous binders considering the aging. Moreover, their relation to functional groups determined by FTIR analysis is summarized based on the available studies.

Chapter 3 presents the details of base binders and WMA additives used in the study, and a brief description of physical and rheological experiments is given. The focus of this chapter is mainly given to the weight-based SARA setup and method. In addition, a small explanation of FTIR analysis is also made within this chapter.

In Chapter 4, the results of the analyses implemented throughout the study have been examined and discussed. The first section investigated the physical, rheological, and chemical properties and their link to unmodified bituminous binders. The second section examined the physical, rheological, and chemical properties and their relations for binders modified with WMA additives.

Chapter 5 explains the results obtained from the analyses, and recommendations for future studies are also provided.

CHAPTER 2

LITERATURE REVIEW

The chemical properties of bituminous binders affect their physical properties, rheological properties, and asphalt mixture performance. Various techniques have been developed to fractionate bituminous binders into SARA fractions, which are Saturate, Aromatic, Resin and Asphaltene. This section discusses the techniques used in the literature to determine the SARA fractions of bituminous binders, and the effects of SARA fractions on the physical, rheological and performance of bituminous binders.

2.1 Separation of Chemical Fraction of Bituminous Binders

Bituminous binders are mostly made of hydrocarbons (Rahimi & Gentzis, 2006). Although they are primarily composed of hydrogen and carbon atoms, in the range of 90-95%, they also contain around 5-10% of different atoms in their structure. These different atoms are classified in two groups: heteroatoms and metals (Nelson, 1968; Jones, 1992).

The first group, heteroatoms, include nitrogen, sulfur, and oxygen atoms. They polarize molecules and increase their interaction with other molecules. Some weak bonds, such as hydrogen bonding, are formed due to these interactions. Despite their low percentage of heteroatoms, these weak bonds specify physical and chemical properties of the bituminous binder (Redelius, 2015). It should also be noted that the percentage of heteroatoms varies depending on the crude oil source of the bituminous binder.

The second group, metal molecules, are less than 1% present in bituminous binders. However, they can be influential when the bituminous binder is exposed to aging. Also, the metal atoms are like the fingerprint of the bituminous binder. Thus, the abundance or quantity of metal molecules can provide information about the source of the crude oil from which the bituminous binder was obtained. Consequently, the chemical composition, hence the physical properties and rheological characteristics depend on the crude oil source (Jones, 1992).

Furthermore, in the publication of The Strategic Highway Research Program (SHRP) 1990 Strategic Planning Document released in 1990, it has been also reemphasized that the physical properties of the bituminous binder influence its chemical fractions. Considering this information, although the chemical composition of bituminous binders is important, physical and rheological properties are used to classify bituminous binders.

In summary, bituminous binders have a complex chemical composition and contain many types of molecules, each in very small quantities. Due to the complexity of its chemical components, the difficulty of analyzing each organic component, and the inadequacy of techniques, it is very challenging to separate bituminous binders into chemical constituents (Redelius, 2006; Jennings et al., 1992). To simplify this complex molecular structure, bitumen binders are separated based on certain chemical properties, including molecular size distribution, polar characteristics, acid-base properties, etc. (Sakib & Bhasin, 2018). For this purpose, several techniques are used in the literature, including Fourier Transform Infrared Spectrometry (FTIR), Nuclear Magnetic Resonance (NMR), Gel Permeation Chromatography (SEC) or Size Exclusion Chromatography (GPC), and Atomic Force Microscopy (AFM). All these techniques somehow allow for the understanding of the bituminous binder at the molecular level. FTIR is used to determine the bituminous binder's functional groups and chemical bonds, while NMR is used for structural characterization like carbon and hydrogen type determination. Additionally, GPC or SEC enables the determination of the molecular weight distribution, while AFM is used for surface morphology and molecular

interaction (Petersen et al., 1993; Zhang et al., 2020). In addition to these techniques, the Ion Exchange Chromatography (IEC) method separates bituminous binders into neutral, acidic, and basic components (Petersen et al., 1993).

Instead of the abovementioned techniques, the polar characteristics of bitumen binders are more influential than other chemical properties in evaluating asphalt performance (Redelius & Soenen, 2015; Sakib & Bhasin, 2016; Sreeram et al., 2019). Also, earlier studies indicate this approach as easy and practical (Sakib & Bhasin, 2018; Jones, 1992). When considering the polar characteristics, bituminous binders are initially separated into asphaltene and maltene fractions.

Asphaltene is a dark black fraction with a high hydrogen/carbon ratio. It is insoluble in n-heptane and n-pentane class solvents but soluble in solvents like toluene and benzene. The fraction that dissolves in pentane or heptane solvents is called maltene, and it is described as a lighter-colored fraction with a lower molecular weight than the asphaltene fraction (Speight, 2006; Traxler, 1936; Yarranton & Masliyah, 1996; Speight, 2006). The maltene fraction is divided into three saturate, aromatic, and resin fractions (Yarranton & Masliyah, 1996). The polarity-based fractions of bituminous binders are defined as Saturates (S), Aromatics (A), Resins (R), and Asphaltenes (A), collectively referred to as SARA (Corbett, 1969; Lesueur, 2009). While the saturate fractions are colorless, the color of resins are described as dark black in color like the asphaltene, and the color of aromatics varies between the yellow and red. Saturates and aromatics are in liquid form, whereas asphaltene and resin fractions are solid fractions in nature (Corbett, 1969). While saturate and aromatic fractions have similar bonds and functional groups, the resin and asphaltene fractions have similar transmittance peaks (Zhang et al., 2015). The content of aromatic and resin fractions in the bituminous binder is typically higher than that of saturate and asphaltene fractions. The amount and molecular structure of the saturate fraction within the bituminous binder vary depending on the chemical composition of the crude oil from which the bituminous binder is obtained and the processing method of the crude oil (Gawel & Czechowski, 1997). Furthermore, in terms of polar characteristics, the most polar fraction is the asphaltene fraction, followed by the

resin fraction; the aromatic fraction has lower polarity than resin, and the least polar one is the saturated fraction (Yarranton & Masliyah, 1996).

The weight distribution of SARA fractions has been investigated in numerous studies in literature. Corbett (1969) revealed that even if two different sources of bituminous binders have the same softening point and penetration value, their chemical compositions can still differ due to the crude oil origin. Similarly, the SHRP researchers investigated the SARA fractions of 32-bituminous binders, and it was observed that the SARA fractions of bituminous binders changed because of the crude oil source. Therefore, it is not possible to specify a range of the weight distribution of SARA fractions (Mortazavi, 1993). In other words, the weight distribution of SARA fractions can significantly vary when bituminous binders are obtained from different crude oil sources (Corbett & Merz, 1975; Mirwald, 2020; Plug et al., 2022; Santagata et al., 2009). Thus, the origin of crude oil should be considered as a crucial factor considering the advances in additive sector.

2.2 Methods for Separating Bituminous Binders into Polar Fractions

Initially, the bituminous binder is fractionated based on polarity into asphaltene and maltene fractions, followed by the further separation of the maltene fraction into saturate, aromatic, and resin fractions. These two stages have been examined separately in the following sections.

2.2.1 Separation Process of Asphaltenes and Maltenes

In the literature, various methods are used for the separation of asphaltene and maltene fractions. These methods take advantage of the insolubility of asphaltene in certain chemical solvents. For the first time, Hubbard and Stanfield (1948) separated asphaltene and maltene fraction from the bituminous binder. In this study, 1.25-1.50 grams of the bituminous binder is initially softened, and subsequently 40 mL of n-pentane is added for every gram of the binder in a tube. Then, this tube is placed in

a 15.6°C water bath, stirred at 2500 rpm for 10 minutes, and the sample is still left for 12 hours after these processes. After 12 hours period, the tube is placed back in the water bath for 20 minutes and stirred for extra 10 minutes. This sample is centrifuged for 5 minutes at a force equivalent to 975 times gravity, and clean pentane is added. These steps are repeated three more times, and after the repetitions, the solution is filtered using filter paper and poured into a weighted flask. Eventually, asphaltenes are separated through filtration and dissolution methods (Hubbard & Stanfield, 1948).

Another method, known as the “Corbett method,” is also used to separate the fractions of the bituminous binder and holds an important place in literature. In this method, 100 mL of n-heptane per gram is added for bituminous binders ranging from 10 to 15 grams. Corbett explained the use of n-heptane as a solvent as follows: when a high dilution ratio paraffin solvent is used, there is a molecular type and distribution inequality between the solvent and asphaltene, causing the asphaltene fraction to precipitate. Like Hubbard and Stanfield's study, the mixture of bituminous binder and n-heptane solvent is stirred and heated overnight, and then the asphaltene fraction is separated using filter paper (Whatman No.1) (Corbett, 1969). The method used by Corbett is almost identical to the asphaltene separation section used in ASTM D4124 Standard Test Method for Separation of Asphalt into Four Fractions.

Furthermore, there are some standards available for separating the asphaltene fraction from crude oil or bituminous binders using gravimetric adsorption chromatography, which are ASTM D4124-09 (2018), ASTM D3279-19, ASTM D2007-19, ASTM D6560-22 and further discussed in the following sections.

2.2.1.1 ASTM D4124 Standard Test Method for Separation of Asphalt into Four Fractions

The ASTM D4124 (2018) is commonly used to separate asphaltenes. It can be applied to any petroleum asphalt. For the beginning of the separation method,

approximately 2 grams of bituminous binder is used to separate asphaltene fraction. 100 ml of iso-octane (2,2,4-trimethyl pentane) is added per gram of the binder. Then, the mixture is stirred and heated until the solution refluxes, with a reflux time specified as 2 hours for the bituminous binder. However, if modified or air-blown asphalt is to be used, it is recommended to reflux for 3 hours. After the reflux process, the solution is stirred at room temperature for 2 hours, and an additional 2 hours is allowed for the solution to settle down. For the filtering process, a Büchner-style fritted glass funnel (60 ml ASTM 10 to 15 μ L medium porosity) is used. During filtration, iso-octane is poured into the funnel until the solution becomes colorless, and then the funnel is heated in an 80°C nitrogen gas-purging oven. Following two- or three-hour cooling period, the weight of asphaltene is determined.

2.2.1.2 ASTM D3279 Standard Test Method for n-Heptane Insoluble

The ASTM D3279 (2019) standard is used for crude oil with a cutback temperature of 343°C or higher, which generally applies to solid and semi-solid petroleum asphalts, gas oils, and heavy fuel oils that contain very little or no mineral matter. In this standard, the weight of material to be tested varies according to the type of material. For air-blown asphalt, 0.5-0.6 grams of sample are used, while for asphalt paving binders and crude residues, 0.7-0.8 grams of sample are used. Additionally, 1.0-1.3 grams of sample are used for gas and heavy fuel oils. 100 ml of n-heptane is used for each gram of sample. The mixture is heated on the magnetic stirrer hot plate while under the reflux condenser. Reflux and mixing duration has been determined as 15-20 minutes for paving binders, fuel oils, gas oils, and crude oils, whereas it is set as 25-30 minutes for air-blown asphalts, followed by approximately 1 hour of cooling at room temperature after the designated time. Then, a filter pad inside the crucible with a diameter of 44 mm is wetted with an n-heptane solution. The mixture is passed through the filter by gently heating it on a hot plate and applying a slight vacuum. After this stage, a 10 ml of n-heptane solvent is passed through the filter about three times for the remaining particles to precipitate on the filter. Then, the

crucible is dried for 30 minutes at $110\pm 5^{\circ}\text{C}$ in an oven and the amount of asphaltene fraction is determined.

2.2.1.3 ASTM D2007 “Standard Test Method for Characteristic Groups in Rubber Extender and Processing Oils and Other Petroleum-Derived Oils by the Clay-Gel Absorption Chromatographic Method”

ASTM D2007 (2016) standard is also commonly used in literature for the separation of asphaltene fraction. This standard is used for processed oil samples with a boiling point of at least 260°C . The sample to be fractionated is adjusted to approximately 10 ± 0.5 grams, placed in a 250 ml flask, and then 100 ml of n-pentane is added and stirred. The prepared mixture is first heated and stirred in a water bath, then left at room temperature for 30 minutes. For the filtration process, a 60 ml n-pentane solution is passed through filter paper in a 125 mm borosilicate filter funnel with a 15 cm filter paper. Then, the n-pentane is evaporated using a hot plate, and the weight of the asphaltene fraction is determined by weighing.

2.2.1.4 ASTM D6560 Standard Test Method for Determination of Asphaltenes (Heptane Insoluble) in Crude Petroleum and Petroleum Products

The ASTM D6560 standard is typically used to determine the asphaltene content in crude oil topped up to 260°C , diesel fuel, motor oil, residual fuel, bitumen, and crude oil. In this standard, if the expected asphaltene content of the sample is below 25% w/w, 30 mL of heptane is added for every gram of the sample. On the other hand, if the expected asphaltene content is above 25% w/w, the minimum amount of heptane to be used is 25 ml per gram. After the sample and heptane mixture are prepared, the solution is boiled under reflux for 60 ± 5 minutes. Then, it is sealed with a plug and left in a dark place for 90-150 minutes. Filter paper is placed, and the solution is poured onto the filter paper without stirring. The residue at the bottom of the solution

is rinsed using warm n-heptane. The solution is refluxed again for 60 minutes at a rate of 2 to 4 drops per second. Then, 30-60 ml of toluene solvent is added, and reflux is continued until the filter paper is clean. The contents inside the solution flask are transferred to new flask. The used old flask is cleaned completely by adding up to 30 ml of toluene, and the contents are transferred to the new flask. Toluene is evaporated by boiling or under a nitrogen atmosphere using a rotary evaporator and the amount of asphaltene fraction is weighed.

2.2.1.5 Comparison of Methods

The abovementioned ASTM standards and studies indicate that a specific solvent and filtration process are used to separate the asphaltene fraction within bituminous binders or petroleum products. The methods are summarized in Table 2.1.

Table 2.1 Summary of the separation methods of asphaltene fraction

Method	Reagent	Reagent/sample ratio	Filter Type	Reflux
Hubbard and Stanfield (1948)	n-pentane	1:40	Pyrex Gooch crucible with porous disk bottoms (40mm diameter)	
Corbett Method (1969)	n-heptane	1:100	Whatman No. 1 paper (11 µm)	
ASTM D4124 (2009)	iso-octane	1:100	Büchner-style fritted glass funnel (60 ml ASTM 10 to 15 µL medium porosity)	+
ASTM D3279 (2019)	n-heptane	1:100	Bitumen crucible or Gooch crucible with a diameter of 44 mm	+
ASTM D2007 (2016)	n-pentane	1:100	125 mm borosilicate filter funnel and 15 cm filter paper	
ASTM D6560 (2012)	heptane	1:30 or 1:25	Whatman Grade 42, 110 mm, or 125 mm diameter.	+

2.2.2 Separation process of maltene into saturate, aromatic, and resin

Maltene fractions of bituminous binder are also analyzed based on their polarity-weight distribution through various techniques. Generally, the maltene fraction is separated using the chromatography base methods utilizing silica and/or alumina column with solvents in the range of non-polar to high polarity. While the saturate fraction is separated using nonpolar solvents, the solvent used to separate the aromatic fraction should be of less polarity than the solvent used to separate the resin fraction (Panda et. al., 2007). In the literature, the techniques commonly used to separate the maltene fraction of bituminous binder into polarity-based fractions can be listed as Gravimetric Adsorption Chromatography, Thin Layer Chromatography-Flame Ionization Detection (TLC-FID), and High-Performance Liquid Chromatography (HPLC) (Boysen & Schabron, 2013).

2.2.2.1 Gravimetric Adsorption Chromatography

Gravimetric adsorption chromatography is a method used in the separation of maltene fractions of bituminous binder, guided by standards ASTM D4124 and ASTM D2007. ASTM D4124 is one of the common methods used to separate bituminous binders into polarity-based SARA fractions in the literature. In this standard, a glass-column and solvents are used to separate the maltene fraction of the bituminous binder into SAR fractions. All solvents used in the standard should be 99.9% HPLC grade, except trichloroethylene which should be in ACS grade. As specified, the volume of the column is 124 cc, its length is 70 cm, and its radius is 1.5 cm. Inside the column, 110 grams of calcined alumina with a dry packing density of 0.90 g/cc are added. After the setup preparation, the test is initiated with the pre-washing stage, which involves wetting the calcined alumina with approximately 70 ml of n-heptane. Throughout the experiment, a cooling/heating circulator is used to stabilize the temperature of the column to keep it at 25°C. Additionally, a pump is employed to provide the solvent flow from the column, and the pump's power is

adjusted to 3 ml per minute. A 25 ml maltene fraction is passed through from the fully wetted column, followed by 5-10 ml of n-heptane solvent to rinse the maltene fraction. Erlenmeyer flasks that collect the sample droplets from the column are numbered and replaced, and a UV detector is used to distinguish between the fractions. It should be noted that the UV detector should be capable of monitoring absorbance changes in the range of 350-400 nm wavelength. After loading the maltene fraction to the column, 150 ml of n-heptane and 33 ml of toluene mixture are passed through to separate the saturate fraction. While passing the solvent, the fluorescence band is monitored, and the Erlenmeyer flask under the column is changed according to the fluorescence band levels. Once the saturate fraction is separated, 100 ml of toluene and 75 ml of a 50:50 mixture of toluene and methanol solvents separate the aromatic fraction. Finally, 150 ml of trichloroethylene solvent is poured into the column and the resin fraction is separated.

In ASTM D2007, the maltene fraction is separated into SAR fractions using columns and solvents, like ASTM D4124. However, a Clay-Gel Absorption Chromatographic method is utilized, and the solvents used in the procedure are pentane, acetone, and toluene, with a minimum purity of 99% specified for pentane and reagent grade minimum purity specified for acetone and toluene. Different than ASTM D4124, clay is added in addition to silica-alumina inside the column. A chromatographic tube with a length of 310 ± 10 mm and a diameter of 48 mm is used. At the bottom of the column, a gel containing 50 grams of clay is placed, followed by 200 grams of silica gel, and finally, 100 grams of clay are positioned on top. The maltene sample fractionated amounts to 10 grams \pm 0.5 grams. Initially, this sample is dissolved in 25 ml of n-pentane. There should be no precipitation in the solution; if it occurs, it indicates that the asphaltene fraction is not successfully separated from the maltene fraction. Then, 25 ml of n-pentane is added to the column, and the poured n-pentane is expected to sufficiently penetrate to the clay. Once the clay is adequately saturated with n-pentane, the 25 ml of mixture is poured into the column. After that, n-pentane is added to the flask and poured into the column again. Following these steps, the walls of the column are thoroughly washed with n-pentane. When the washing is

completed, pentane solvent is added to separate the saturate fraction, and the saturate fraction is collected with a flask placed under the column. After the saturate fraction is separated, the two columns are separated from each other, and the upper column is washed with n-pentane and a 50:50 mixture of toluene and acetone solvents is used to separate the aromatic fraction. The solvent should be added to the solution dripping into the flask from the column until it becomes colorless, and the amount of solvent added usually does not exceed 300 ml unless there is a special circumstance. The aromatic fraction separated with toluene and acetone is stirred several times in each flask and left to stand for about five minutes, during which, at the end of the waiting period, a portion settles to the bottom while another portion remains liquid above. The liquid portion is poured off, and approximately 10 grams of anhydrous calcium chloride are added to the remaining precipitate, stirred for 30 seconds, and allowed to settle for at least 10 minutes. Subsequently, the solutions are separated using filter paper and approximately 25 ml of n-pentane solvent. An extra 10-15 ml of n-pentane is also used to wash the filter paper. The residue remaining from the toluene-acetone mixture is used to calculate the resin fraction. In addition, the aromatic fraction is determined based on the difference or isolation.

2.2.2.2 High Pressure Liquid Chromatography (HPLC)

High-Pressure Liquid Chromatography (HPLC) method used in analytical chemistry splits non-volatile materials into fractions with the help of pressure (Robards et al., 2022). Due to the absence of a fast chemical composition determination method in the petroleum industry, Suatoni (1979) developed the HPLC method for the first time to address this deficiency. This method provides an advantage in terms of its applicability to any material soluble in a liquid mobile phase (Heshka, 2021). Moreover, the HPLC method is advantageous in terms of separating materials with boiling points above 500°C into their components; indeed, petroleum residues mainly consist of components with high boiling points (Østvold, 1998). In the first study conducted on the HPLC method (Suatoni et al., 1975), the first step involves

the separation of the fraction insoluble in hexane solvent, representing the asphaltene fraction in the bituminous binder. The hexane and bituminous binder solvent in a 50:1 ratio is stirred for about one and a half hours at 40°C. The insoluble fraction (asphaltene) is separated upon reaching room temperature using a Millipore filter. After the separation process, 20 µl of the solution is used for chromatography. In the following stages, a column (10 microns of Porasil) is used. Initially, the saturate fraction is separated, aromatics are obtained by using backflushing, and the final fraction is the resin fraction, remains within the column. The resin fraction is determined by subtracting the final quantity from the initial quantity. With the chromatographic method, a flow of 2 ml per minute is provided, completing the process in 8 minutes. The advantages of this method are that it enables separation in a short time with a small number of samples. However, it has been developed over time due to its inadequacy separating the maltene fraction into subfractions.

In the HPLC method improved by Gayla and Suatoni (1980), like in its initial version, the bituminous binder is mixed with hexane to separate the asphaltene fraction of the bituminous binder. The separation process is performed by pulling the solution through a 0.45 µ Millipore filter (filter type UH) using a vacuum. The saturate and aromatic fractions are first separated from the solution from which the asphaltene fraction has been removed. For this stage, a FeCl₃-Clay column is used, and the saturates and aromatics are separated by backflushing and collected up to 200 ml of eluent containing saturates and aromatics. For the remaining resin fraction in the column, a mixture of acetone and methylene chloride in a 1:1 ratio, about 200 ml, is added to the column, and the separation process is completed.

In another study (Aske et. al, 2001), two silica-NH₂ columns were used; the reason is that the first column retains the resin fraction while the second column retains the aromatics, and the saturate fraction is eluted from these columns. Initially, the bituminous binder is mixed with 120 ml of hexane and then filtered using a 0.45 µ Millipore filter to separate maltene fraction. The saturate and aromatic fractions are

separated with n-hexane at a flow rate 8ml/min from the column, while the resin fraction is separated with trichloromethane through backflushing. The aromatic and resin fractions can be observed with the UV detector response, while the saturate fraction can be observed with the IR detector response. The detector material used in the HPLC method is selected based on properties, i.e. fluorescence, UV-visible absorbance, and conductivity (Robards et. al., 2022). For the SARA fractions of petroleum products, the saturate fraction cannot be observed by the UV detector due to its high energy demand and being unobservable in the 200-400 nm range. Therefore, an IR detector is used to observe the saturate fraction. As for the asphaltene, aromatic, and resin fractions, they occur at around 300 nm, and a UV detector is sufficient (Woods et al., 2004; Karevan et al., 2021).

In another study (Karevan et al., 2021), three columns are packed with poly (tetrafluoroethylene PTFE), cyano, and silica, in a sequence. Initially, a pentane solution is used for the separation of asphaltene fraction in the PTFE column. After this stage, the resin fraction is separated in the cyano column, while the aromatic fraction remains in the silica column, and the saturate fraction cannot be retained in either of these columns. To obtain the saturate fraction, a propane gas flow is applied into the column, and the pentane solvent inside the column is removed. For the aromatic and resin fractions, both are separated using a toluene solvent and observed with a UV detector. Furthermore, this study was revised a year later, and the column type was changed, in which ZORBAX RX-SIL is used instead of the silica column, and ZORBAX CN is used instead of the cyano column, while the PTFE column is also used in this study. The ZORBAX RX-SIL and ZORBAX CN columns are more densely packed than the previous ones. In the study, the asphaltene fraction is dissolved in toluene and separated with the help of PTFE. The aromatic fraction is retained in the ZORBAX RX-SIL column, while the resin fraction is retained in the ZORBAX CN column. Like the previous study, the saturate fraction cannot be observed, but in this study, ethane gas is used instead of propane gas. The reason for using ethane gas is that due to the increased column density in this study, higher pressure is required to remove the solution inside the column (Karevan et al., 2022).

On the other hand, the HPLC method, which does not have a specific standard, is more user-focused because features such as the solvent type of selection, the amount of solvent, the number of columns, the column content, and the analysis time vary from one operation to another. Considering the previous studies, it is inferred that the HPLC method provides results faster than ASTM methods, moreover it is reproducible and precise. However, although the stage from sample injection to fraction collection in the HPLC system is completed in a short time, the re-equilibration times of the columns take a considerable amount of time. At the same time, the sample preparation time is also lengthy, and considering these, the HPLC method can be interpreted as impractical. To shorten the time, there is a need for a mechanism in the HPLC system that can ensure flow control and backflush valves, which significantly reduce the column's re-equilibration time (Grizzle et al., 1986). In the HPLC method, the asphaltene fraction is not separated chromatographically but is typically separated using a chemical solvent with the help of a PTFE column. To separate the asphaltene fraction chromatographically, a heptane mobile phase is used to precipitate it from the residues in the column, referred to as the asphaltene determination (AD) method (Schabron et al., 2010).

In the study conducted by Boysen and Schabron (2015), the fractions of petroleum products are separated using HPLC and AD methods, which is named HPLC SAR-AD. Four columns are used in this study, which are PTFE, glass beads, aminopropyl bonded silica gel, and silica gel. The silica gel column has been kept at 120°C overnight and activated. For chromatographic analysis, 2 mg of the petroleum product is mixed with chlorobenzene (ml) at a ratio of 1:10 to prepare a solution. The mixture is passed through a 0.45 µm syringe filter, and after filtration, 20 µl aliquot of the solution is loaded onto the HPLC. In the study, the solvents used are heptane, cyclohexane, and methylene chloride: methanol (98:2), respectively. After loading the sample into the HPLC, the asphaltene fraction precipitates in the PTFE column, and the saturate fraction dissolves in heptane, passing through the ground PTFE, glass beads, aminopropyl, and activated silica columns. The aromatic fraction is collected in the activated silica column. Resins with the highest surface energy are

collected in glass beads, while other resins are collected in the aminopropyl column. The asphaltenes retained in the PTFE column are separated into highly alkyl-substituted asphaltene components, less alkyl-substituted peri condensed aromatic asphaltene components, and finally pre-coke peri condensed aromatic asphaltene components. To perform this separation, the asphaltenes are first dissolved in cyclohexane, then in toluene, and finally in methylene chloride: methanol (98:2 v: v). Toluene is passed through the activated silica column to separate the retained aromatic fraction. In the final stage of the method, backflushing is performed, passing methylene chloride: methanol (98:2 v: v) through the aminopropyl and glass bead columns. The columns are passed through using toluene and then heptane solvents to prepare the entire system for other chromatographic analyses. Additionally, the method uses two variable wavelength absorbance detectors, one capable of observing 500 and 700 nm wavelengths and the other being an evaporative light scattering detector (ELSD). Six peaks are obtained from ELSD chromatography results (aromatic, saturate, highly alkyl-substituted asphaltene components, less alkyl-substituted peri-condensed aromatic asphaltene components, pre-coke peri-condensed aromatic asphaltene, resin). The peak areas of the obtained points are considered and analyzed in direct proportion to the amount of material. The study consists of different columns that work together and are interconnected to create an integrated modular system. Consistent results are obtained when considering the physical properties and chemical composition of the bituminous binders used in the method, and the system is highly repeatable.

One of the recent studies by Adams et al. (2023) utilize SAR-AD fractionation, a similar method to the Boysen and Schabron (2015) and analyze 8 samples of heavy oil. It is also reported that the SAR-AD fractionation is a repeatable method for the separation of different and complex chemical structures, but it was noted that some compounds did not correspond to a single fraction that means fractions are not pure. Diverging from other methods, a completely automated HPLC method has been developed for the separation of SARA fractions of bituminous binders, termed automated multi-dimensional HPLC (AMD-HPLC). In this approach, unlike

conventional HPLC methods, there is no prior asphaltene fractionation before loading the sample onto the HPLC system, there is no lengthy sample preparation, it is an automated and more efficient process. In this method, a column composed of one cyano and one silica is used. 0.02 grams of petroleum product are dissolved in a 300 μ L solution consisting of 15% methanol, 15% acetone, and 70% chloroform. Once the solution is prepared, it is loaded into the equipment. The process consists of four steps. In the first step, hexane is passed through to obtain the saturate fraction. Secondly, a mixture of hexane and chloroform (94:6 v: v) is used to obtain the resin. In the third step, a mixture of 15% methanol, 15% acetone, and 70% chloroform is prepared, and the asphaltene fraction is eluted. In the final step, aromatics are obtained with the help of a chloroform solution. However, even though the method performs well, the separation of asphaltene resin fractions could be improved, and attention should be paid to the quantification of volatile substances (Bissada et al., 2016).

2.2.2.3 Thin Layer Chromatography-Flame Ionization Detector

One of the powerful and well-established methods in literature is the thin-layer chromatography Flame-Ionization Detector (TLC-FID) to separate petroleum products into their chemical components. This method was first used by Padley in 1968. Initially, a thin silica glass coated with silica gel is used to perform thin-layer chromatography on the asphalt binder. Then, the separated fractions are quickly passed through a glass rod and burned with pure hydrogen provided by the detector for identification. In the study, the most significant contribution of the method is explained as the ability to define the volatility of materials or rather organic compounds.

Furthermore, the IP469 standard is used to define the chemical composition of petroleum products, with the asphaltene fraction not being identified in this separation process. Specifically, the separated fractions are saturate, aromatics, polar (1), and polar (2). Polar (1) fraction is defined as a fraction with a lower molecular

weight containing nitrogen, sulfur, and oxygen atoms, and it dissolves in a mixture of dichloromethane and methanol solution. On the other hand, polar (2) is defined as a fraction with a high molecular weight that is not dissolved by the solvents used in the standard. Although it closely resembles the asphaltene fraction, it is not referred to as the asphaltene fraction in IP469. This standard encompasses products with a minimum boiling point of 300°C and distillate products alongside petroleum products. The standard employs a device called Iatroscan, a single commercial instrument. Initially, the part known as TLC covers thin bonded layers, which consist of solvent and absorbent layers. The absorbent layers are referred to as the stationary phase, while the solvent layers are known as the mobile phase. In the FID, organic compounds are burned in a hydrogen/air flame to ionize and load electrons. Before starting the experiment, ten quartz rods are prepared and placed inside a frame. The FID flame scans the quartz rods to activate and clean them. This process is performed at least twice without recording, and the third scanning process is recorded. Furthermore, three tanks are prepared, each filled with approximately 60-100 ml of solvent. The first tank (A) is filled with n-heptane solvent, the second tank (B) with an 80:20 mixture of toluene: n-heptane, and the third tank (C) with a 95:05 mixture of dichloromethane: methanol. After the tanks and frame are prepared, a sample of 100±10 mg is prepared for chromatographic analysis. 5±0.1 ml of dichloromethane solvent is added to the sample using a pipette and mixed. The frame containing quartz rods is placed on a perplex staining guide or lined paper. A 1 µL solution is loaded onto each quartz rod, and the frame is dried in an oven with a temperature of 50-70°C for a minimum of 2 minutes, followed by approximately 2 minutes for it to return to room temperature. Initially, the frame is placed in Tank (A), allowing it to move from the application point to the quartz rods by approximately 100±5 mm. It is then removed, dried for 5 minutes in the 50-70°C oven, and allowed to return to room temperature. Subsequently, the frame is placed in Tank (B), allowing it to move from the application point to the quartz rods by approximately 50±5 mm. The drying process is performed in the same manner as before. Thirdly, it is placed in Tank (C), with a designated movement range of 20±2 mm, and the drying process is repeated.

After being in the tanks with three different solvents, the quartz rods are inserted into the TLC-FID analyzer, which detects four distinct peaks. Each peak corresponds to the saturate, aromatic, polar (1), and polar (2) fractions, respectively. A baseline is drawn just below the saturate peak and just above the polar (2) peak, and the fraction percentages are calculated from areas. While the TLC-FID method is used in the literature to separate petroleum products into SARA fractions, there are variations among studies, primarily in terms of sample weight, the solvent used to liquefy the sample, and the solvents assisting in the fractionation process.

2.2.2.4 Comparison of Maltene Separation Methods

In general, three methods are employed to separate the saturate, aromatic, and resin fractions of the bituminous binder, and these three methods have been revised in this section. In the gravimetric adsorption chromatography and HPLC methods, the fraction is initially separated through dissolution, while dissolution is not implemented in the TLC-FID method. Additionally, when evaluating the quantities of bituminous binder (sample weight) for the analysis, it is observed that much smaller samples are used in the TLC-FID method compared to the other methods. Hence, gravimetric adsorption chromatography is not considered an appropriate method due to the excessive usage of solvents and absorbents i.e. alumina, silica, or clay (Kharrat et al., 2007). Moreover, in a study (Barman, 1996), SARA fractions were compared using both clay-gel adsorption chromatography (ASTM D2007) and the TLC-FID method on the same sample. According to the findings, it was indicated that ASTM D2007 does not always yield pure fractions, i.e., the samples undergo incomplete recovery. On the other hand, TLC-FID offers advantages such as providing faster results, using smaller samples, utilizing less solvent, and yielding more consistent results compared to ASTM D2007. Additionally, it was explained that the solvents and quartz rods used in the TLC-FID method can be reused, whereas the solvents in the ASTM method cannot be recovered. In contrast, Masson et al. (2001) explained that the rods used in the TLC-FID technique undergo aging. It was

even demonstrated that the aged chroma-rod leads to an increase in the resin fraction content. Also, it was discovered that chroma-rod aging contributed to a 2-5% difference in the results. In the same study, it was proven that if factors such as temperature, humidity, and time are carefully monitored during chromatographic analysis, the reproducibility of the TLC-FID analysis is 10. Additionally, Fan & Buckley (2002) used six samples, each separated into SARA fractions by applying the TLC-FID, HPLC, and ASTM D2007 methods. It was observed that even with the same sample, each of the three methods yielded different results, leading to the conclusion that the proportions of SARA fractions vary depending on the applied method. Additionally, despite being the fastest separation method, it is explained that a significant portion of the saturate and aromatic fractions are lost in the TLC-FID method since before the flame ionization detector since it contains a lot of volatile material. Furthermore, it is stated that the results of the HPLC and ASTM D2007 methods are closer to each other than to TLC-FID. Moreover, in terms of the duration of the experiment, ASTM D2007 takes longer than HPLC. Therefore, HPLC is a more practical separation method. When the advantages and disadvantages of these methods are evaluated, Sakib and Bhasin (2018) have developed a new weight-base SARA method. It is aimed to develop a fast, economical, and reproducible alternative method. The method used in this thesis follows Sakib and Bhasin's (2019) procedure and is broadly discussed in Section 3.4.

2.3 Solubility Parameters of the Bituminous Binder

When examining the methods utilized for the fractionation of bituminous binders into their chemical constituents and reviewing the current literature, it is observed that the main difference is the solvents used in different studies. Therefore, the solubility parameters should also be examined (Sakib & Bhasin, 2019). To comprehend the chemical structures of bituminous binders, it is imperative to investigate their molecular interactions, as a connection exists between the solvents

and molecular interactions. This implies that the utilized solvents can influence the strength of these interactions (Redelius & Soenen, 2015).

The solubility parameters of bituminous binders were initially characterized by Hildebrand (1936), who explained that the solubility parameter indicates that if two substances have similar cohesive energies regarding type and magnitude between their particles, they will dissolve. This implies that the solubility parameters of two substances that can mix with each other are also similar. Hansen Solubility Parameters: A User's Handbook (2007) investigated the Hildebrand solubility parameters of 15 different bituminous binders using 42 different solvents. In the study, when the binder is completely dissolved in a solvent, the solvent is classified as good solvent, while other solvents were considered poor solvents. However, it should be noted that the calculated Hildebrand solubility parameters can be in the same range for both good and poor solvents. For instance, toluene, known to dissolve bituminous binders and used in certain separation methods, is considered a good solvent. However, ethyl acetate, which has a similar Hildebrand solubility parameter as toluene, is a poor solvent. This confusion may arise from the fact that polar interactions, pi-pi bonding, or hydrogen bonding have not been considered in the determination of the Hildebrand solubility parameter, which affects the solubility parameters of these compounds (Laux et al., 1997; Redelius, 2004). Therefore, the Hildebrand solubility parameters are inappropriate for the bituminous binder (Redelius, 2000). The Hansen Solubility Parameter (HSP) is another parameter that provides a more practical approach for defining polar interactions or hydrogen bonding fractions (Redelius, 2004). Therefore, HSP is more appropriate for bituminous binders. In HSP, there are three components: dispersion (D), polar (P), and hydrogen bonding (H). Li et al. (2022) extracted asphaltene and maltene fractions from vacuum residue, and solution behavior was elucidated using 27 different solvents. Table 2.2 presents the solution behavior for the asphaltene and maltene fractions using different solvents. The data reveals that heptane is insoluble for the asphaltene fraction but soluble for the maltene fraction. Other solvents, namely n-hexane, pentane, and methanol, are also incapable of dissolving the

asphaltene fraction. Additionally, it is observed that methanol is the only solvent unable to dissolve the maltene fraction, whereas the remaining solvents exhibit dissolution. In the study, it has been explained that based on the HSP values and solution behaviors for both the maltene and asphaltene fractions, the maltene fraction can dissolve in solvents with strong dispersion forces and weak hydrogen bonds, along with a weak polarity, compared to the asphaltene fraction.

Table 2.2 HSP of the Asphaltene and Maltene Fraction (Li et. al., 2022)

Solvent	δD Mpa ^{0.5}	δP Mpa ^{0.5}	δH Mpa ^{0.5}	δ_{total} Mpa ^{0.5}	Solution	Solution
					Behavior in Asphaltene	Behavior in Maltene
heptane	15.5	0.0	0.0	15.5	insoluble	soluble
n-hexane	14.5	0.0	0.0	14.5	insoluble	soluble
pentane	15.3	0.0	0.0	15.3	insoluble	soluble
toluene	18.0	1.4	2.0	18.2	soluble	soluble
dichloromethane	17.0	7.3	7.1	19.8	soluble	soluble
trichloroethylene	18.0	3.1	5.3	19.0	soluble	soluble
methanol	14.7	12.3	22.3	29.4	insoluble	insoluble

Redelius (2004) utilizing HSP components derived a new parameter named Relative Energy Difference (RED), ratio of two additional parameters, denoted as R_a and R_m . R_a is defined as the difference between the solubility parameters of the bituminous binder and the solvent, and R_m is defined as the maximum solubility parameter difference, in which bituminous binder is still soluble in the solvent. If the RED value is less than 1, it signifies the complete dissolution of the material, and if it is greater than 1, it indicates partial dissolution or insolubility. In Table 2.3, the RED values

for some solvents that are typically used in the SARA fractionating are presented. Based on the table, the asphaltene fraction does not dissolve in heptane, while the saturate and aromatic fractions dissolve completely. The resin fraction is known to be absorbed by the asphaltene fraction (Verdier, 2005). Thus, the RED values for the resin fraction in heptane solvent are greater than 1. In other words, this situation can indicate partial dissolution within the heptane solvent (Park et al., 2022).

Table 2.3 RED values of SARA Fractions (Park et al. al., 2022)

Solvent	RED value of Saturate	RED value of Aromatic	RED value of Resin	RED value of Asphaltene
heptane	0.42	0.84	1.73	2.17
benzene	0.58	0.83	1.28	1.29
toluene	0.46	0.58	0.99	0.99
triethylamine	0.44	0.67	1.25	1.35
dichloromethane	1.00	0.96	0.50	0.64

During the fractionation of the bituminous binder into its polarity-based fractions, the solubility parameter plays a crucial role, particularly in the segregation of the asphaltene fraction, which is commonly isolated as a precipitate. Thus, solvent selection for the fractionation process is determined based on research findings and the existing solubility parameters in the literature.

2.4 The Relationship Between SARA Fractions and Physical Properties of Bituminous Binders

The SARA fractions in bituminous binders' effect on the physical characteristics of the binder (Redelius & Soenen, 2015; Liu et al., 2023; Weigel & Stephan, 2017; Wang et al., 2021). Asphaltene and resin fractions are considered hardening fractions of the bituminous binder, while saturate and aromatic fractions are regarded as softening or plasticizing fractions (Corbett, 1969). Notably, the penetration grade and softening point temperature are directly influenced by the asphaltene fraction

(Zenke, 1977; Aljaafari & Ismael, 2020). As the asphaltene content within the bituminous binder increases, a corresponding decrease in penetration value and an increase in the softening point value are observed. Essentially, a higher proportion of asphaltene within the bituminous binder correlates with enhanced hardening properties (Mangiafico et al., 2016).

The SARA fractions of bituminous binder also affect the viscosity of the bituminous binder since the interaction of the chemical molecules within the bituminous binder and the molecular weights of the fractions influence the viscosity (Redelius & Soenen, 2015). If the asphaltene and saturate fractions are high within the bituminous binder, an increase in the viscosity of the bituminous binder occurs. On the other hand, no relationship is established between the aromatic and resin fractions on viscosity (Glover et al., 1987). Another study by Robertson (2001) indicated that the asphaltene and maltene fractions within the bituminous binder significantly influence the viscosity of the bituminous binder. A bituminous binder with a higher asphaltene content has a higher viscosity, whereas a bituminous binder with a higher maltene content has a lower viscosity (Dealy, 1979; Robertson, 2001). Moreover, in another study, different proportions of the asphaltene fraction were added to the bituminous binder, and changes in the viscosity of the bituminous binder were observed. As a result, while the asphaltene fraction plays a major role, the SARA fractions collectively impact the physical properties of the bituminous binder.

2.5 Aging Effect on SARA Fractions

The weight distribution of SARA fraction changes with the aging of bituminous binders. It is known that the aromatic and saturate fractions decrease, while the resin and asphaltene fractions increase with aging. In other words, when bituminous binder is exposed to aging, liquid components decrease, and solid components increase (Corbett & Merz, 1975). Glover et al. (1987) stated that as the bituminous binder exposed to aging, the molecular size of asphaltene and resin fractions will increase, the molecular size of the saturated fraction will remain unchanged. In

addition, there will be a small change in the molecular size of the aromatic fraction, but there will be a significant change in its quantity. In a study conducted by Hashshenas et al. (2016), it is explained that due to oxidation, the aromatic fraction initially transforms into the resin fraction and then into the asphaltene fraction. However, it is also stated that an increase occurs in both the resin and asphaltene fractions with aging, and there is no considerable change in the weight of the saturate fraction. In another study by Mirwald et al. (2020), the changes in SARA fractions of three different bituminous binders from the 70/100 penetration class obtained from different refineries were examined after short- and long-term aging process. The results showed that the asphaltene fraction within the bituminous binder increased significantly (7%-22%), while similarly, the aromatic fraction decreased considerably (12%-24%). However, the changes in saturated and resin fractions were less pronounced than in the other fractions. The resin fraction within the bituminous binder increased (4%-8%), and the saturate fraction increased (1%-3%). Additionally, in a much more recent study (Ren et al., 2022), the changes in the chemical components of the bituminous binder under aging conditions were also examined. When subjected to aging, bituminous binder undergoes partial oxidation in its aromatic and asphaltene molecules while resisting oxidation in its saturate molecules. Observations reveal that during the bituminous binder's aging process, the aromatic fraction's initial transformation occurs into the resin fraction, followed by its conversion into the asphaltene constituents. Consequently, the aging of the bituminous binder leads to an increase in polar components, namely the asphaltene and resin fractions, while the saturate fraction and the aromatic fraction experience an increase first and then a decrease (Ren et. al., 2022). In summary, according to the reviewed studies, it can be concluded that the asphaltene and resin fractions increase with aging, while the aromatic fraction decreases. Moreover, the saturate fraction either decreases or remains constant as the bituminous binder is exposed to aging. However, according to Robertson et al. (2001), although the asphaltene fraction within crude oil significantly affects its rheological properties, the significance of the asphaltene fraction itself is how it is dispersed by the maltene

fraction, which determines its rheological properties. Therefore, the Gaestel index is used to describe the rheological properties of bituminous binders composed of a colloidal system. This system investigates the dispersed or dissolved state of asphalt micelles within the maltene. The colloidal system of the bituminous binder consists of sol and gel types. The sol type exhibits behavior indicating that if there is sufficient solvent power from resins and aromatics, the asphalt turns entirely into a peptidic state, consequently facilitating good mobility of micelles. Micelles are formed by the combination of resins, which constitute a stabilizing and solvent layer, along with asphaltenes. Gel-type bituminous binders have an irregular and mixed structure due to insufficient aromatics/resin content, preventing the micelles from peptizing (Hunter et al., 2015; Weigel & Stephan, 2018).

As the bituminous binder undergoes aging, it is expected to observe an increase in the Gaestel Index. With the escalation of the index, the asphaltenes peptide less, and the bituminous binder exhibits a gel-type character (Kleizienė et al., 2019; Siddiqui & Ali, 1999). Similarly, as the Gaestel Index decreases, the bituminous binder demonstrates a sol-type character. Moreover, as the Gaestel Index increases, the stabilization of the bituminous binder decreases. Gaestel Index has defined stabilization within the range of 0.22-0.5. If the Gaestel Index exceeds 0.5, it is interpreted that the bituminous binder hardens/ages, while if it is below 0.22, the bituminous binder is interpreted as being softer (Gaestel et al., 1971; Paliukaite et al., 2014; Paliukaite et al., 2015). Therefore, the Gaestel index values calculated using the SARA fractions of the bituminous binder provide information in understanding the rheology of the bituminous binder.

2.6 The Relationship Between SARA Fractions and Rheological Properties of Bituminous Binders

The rheological properties of bituminous binders are directly linked to the polarity of the binder (Redelius & Soenen, 2005; Weigel & Stephan, 2017). Yang et al. (2020) examined the chemical composition of bituminous binders from different

sources and with different penetration grades. It was shown that the complex shear modulus (G^*) increases with the asphaltene and resin fractions in the bituminous binder, while it decreases with saturate and aromatic content increases. Saturates generally have the lowest complex modulus (G^*) at each frequency value, while the resin fraction has the lowest phase angle (δ) value at high-frequency ranges. The reason for the resin fraction having a low phase angle at high frequencies is interpreted as potentially being elastic at high temperatures and brittle at low temperatures. The resin fraction has the best rutting resistance property than other fractions at high temperatures. While aromatics assist in the flexibility of the bituminous binder, the resin fraction provides rutting resistance. Also, the aromatic fraction has been identified as the most susceptible to aging due to carbonyl groups (Ren et al., 2022; Yang et al., 2020). In a study by Sultana (2014) that examines the effects of polar fractions (asphaltene and resin fractions) on stiffness, it is explained that stiffness increases at low frequencies of loading. However, there is not a significant increase in high loading frequencies. Furthermore, having a higher content of asphaltene and resin fractions in the bituminous binder affects stiffness and tensile strength (Ishai et al., 1993). In the bituminous binder, having a high content of saturate and aromatic fractions in its structure also reduces the stiffness and the tensile strength (Sultana & Bhasin, 2014). Generally, when the relation between the chemical and rheological properties of bituminous binder is examined, the significance of the asphaltene fraction within the bituminous binder becomes apparent. The temperature sensitivity is directly correlated with the asphaltene content in the bituminous binder, as well as with the complex shear modulus (G^*) and the phase angle (δ). As the asphaltene content in the bituminous binder increases, the complex shear modulus increases, and the phase angle decreases. Additionally, an increase in the asphaltene fraction within the bituminous binder increases the value of G^* , which indicates stiffness. At the same time, an inverse relationship has been observed for the phase angle. In other words, as the asphaltene content in the bituminous binder increases, the elastic deformation behavior also increases, decreasing the phase angle (Weigel & Stephan, 2018). In another study (Lu &

Isocsson, 2002), the master curves of the bituminous binder were examined, and it was observed that after aging, the complex shear modulus of the bituminous binder increases as the asphaltene content within the binder increases, while the phase angle decreases. Another study examined the chemical properties of PG52-28 bituminous binder from the Ural region in Russia and PG52-34 bituminous binder from Cold Lake in Alberta, Canada. The research investigated the asphaltene content within the bituminous binder, highlighting its significance alongside the analysis of SARA fractions, molecular weight, and chemical composition. The study revealed that the asphaltene content in the Ural bituminous binder is lower than that in Cold Lake, and its correlation with asphaltene content suggests that Cold Lake asphalt would be more resistant to rutting at high temperatures. Additionally, it was explained that low or medium asphaltene content makes the bituminous binder more brittle and stiffer under low or moderate temperatures (Michalica et al., 2008). When the content of the asphaltene fraction in the bituminous binder increases, the elastic deformation behavior increases with aging (Weigel & Stephan, 2017). Furthermore, another study elucidated that SARA fractions influence the bituminous binder's fatigue resistance and healing behavior. The research revealed that an augmentation in asphaltene content results in a reduction of fatigue life. In a study (Glover et al., 1987) examining the effects of SARA fractions on the performance of bituminous binders, it has been found that a high content of asphaltene, and more specifically, a high content of large molecule asphaltene, can lead to pavement cracking in time. In conclusion, there are strong correlations between the rheological properties of the bituminous binder that occur with aging and SARA fractions.

2.7 Warm Mix Asphalt (WMA) Additives

Hot Mix Asphalt (HMA) is a traditional road construction material, which poses serious environmental effects such as emissions, air pollution, energy consumption, etc. To mitigate the adverse effects of HMA on the environment, it is necessary to lower the production and mixing temperatures. The Warm Mix Asphalt (WMA)

technology, produced at a lower temperature in the range of 20-55°C compared to the HMA, is employed to reduce the negative impacts of HMA without affecting or compromising the performance of the asphalt (D'Angelo et al., 2008; Del Carmen Rubio et al., 2013; Rubio et al., 2012). Indeed, it is recognized that using WMA technologies can result in a reduction of up to 30% in fuel energy consumption and emissions (Sargand et al., 2009; Diab et al., 2016; Li et al., 2023; Sukhija et al., 2022; Calabi et al., 2020). Therefore, asphalt production can be achieved at a lower cost (Chowdhury & Button, 2008; D'Angelo et al., 2008; Sukhija et al., 2022). However, to implement WMA technology, certain additives or additional equipments must be used since the properties of the bituminous binder can be enhanced (Milad et al., 2022; Yousefi et al., 2021). Most WMA technologies depend on additives. These additives are classified into three categories: organic, chemical, and foaming processes (Caputo et al., 2020; Rubio et al., 2012). Hence, the influence of these three additives on the properties of the bituminous binder varies.

Initially, the additives categorized as organic commonly comprise waxes such as Fischer-Tropsch wax, Montan wax, and oily amides (Caputo et al., 2020; D'Angelo et al., 2008). The most common organic additives are Asphaltan B[®] and Sasobit[®] (Caputo et al., 2020). The melting temperature of waxes is a crucial criterion in selecting the additive. The choice of wax is determined based on the estimated service temperature of the asphalt. If the wax's melting temperature is lower than the asphalt's service temperature, it can lead to significant permanent deformation (D'Angelo et al., 2008). Organic additives reduce the viscosity of bituminous binders. Moreover, they enhance the performance of the bituminous binder at high temperatures. However, they have tendency to decrease bituminous binder performance at low temperatures (Belc et al., 2021).

The second category of additives are chemical additives. The most common chemical additives are Cecabase, Rediset, and Evotherm. In contrast to organic additives, chemical additives do not affect the viscosity of bituminous binders (Pereira et al., 2018). Chemical additives reduce the friction between the binder and

aggregate, decreasing surface energy. Additionally, they enhance the rutting potential of the bituminous binder (Hurley & Prowell, 2006; Pereira et al., 2018).

The third category is that the foaming additives generally consist of water-containing or water-based additive materials (Belc et al., 2021). The common types of foaming additives are Aspha-min and Advera. Foaming additives enhance the workability of the bituminous binder. As the temperature of the bituminous binder rises, the water within the water-containing additive evaporates, and the vapor remains within the bituminous binder. This can lead to a volumetric expansion of the bituminous binder, reducing its viscosity (Behnood, 2020).

In this study, Sasobit, an organic additive, and Evotherm, a chemical additive, are used; therefore, the literature review is only focused on the use of these two additives.

2.7.1 Effect of Sasobit Additive to the Bituminous Binder Properties

As aforementioned, Sasobit is an organic additive commonly used in WMA applications. It is a wax of Fischer-Tropsch. Although Sasobit is recommended to be used between 0.8% and 3% by weight of the bituminous binder, it is generally added to the bituminous binder at a rate of 1% to 1.5% (Hurley & Prowell, 2005; D'Angelo et al., 2008).

Previous studies indicated that Sasobit usage reduces the penetration value, increases the softening point value, and reduces viscosity (Zhang et al., 2015). Cao & Jie (2011) conducted a study in which a bituminous binder was modified by adding Sasobit additive at a rate of 2%, 3%, 4%, and 5% by weight of the binder. The base binder has a penetration of 71 and a softening point of 49.6. With 2% Sasobit, the penetration of the bituminous binder decreased to 61, and the softening point rose to 66.3°C. At the maximum level of 5% Sasobit, the modified binder had a penetration of 41 and a softening point of 92.8°C. As the ratio of additives increased, the penetration of the binder decreased while the softening point increased. Also, Chen et al. (2023) conducted a study in which they added Sasobit to the bituminous binder

using the WMA additives at proportions of 1%, 3%, and 5% and demonstrated changes in penetration and softening point. The penetration value of the unmodified bituminous binder was 55.7, and when 1% Sasobit was added, it decreased to 42.2. When 3% Sasobit was added, it decreased further to 37.8. These results prove Sasobit's effect on hardening the bituminous binder. Moreover, the unmodified bituminous binder had a softening point of 90°C. The addition of 1% Sasobit increased to 93°C; with 3% Sasobit, it increased to 98.9°C. Furthermore, in a study, as the additive content increased from %2 to %5, there was a decrease in viscosity at 135°C (Jao & Cie et al., 2011). Also, according to Hamzah et al. (2012), the Sasobit additive decreases the viscosity of the bituminous binder. Therefore, the Sasobit additive decreases the viscosity of the bituminous binder.

In a study (Jamshidi et al., 2012), the Sasobit additive was added to three different bituminous binders at rates of 1%, 2%, 3%, and 4%, and the changes in their rheological properties were examined. The Sasobit additive increases the true grade of the bituminous binder and, consequently, the PG grade. It has been demonstrated that the Sasobit additive increases the G^* value at intermediate and high temperatures as the additive ratio increases while it decreases the phase angle (δ). Therefore, the Sasobit additive increases the $G^*/\sin(\delta)$ value, thereby enhancing the rutting resistance of the Sasobit binder. In another study (Julaganti et al., 2017), three different proportions (%1, %2, and %3) of Sasobit additive were added to the bituminous binder, and the rheological properties were investigated. It has been proven that the Sasobit additive increases the true grade of the bituminous binder and enhances its rutting resistance. Thus, it can be concluded that Sasobit enhances the rutting resistance of the bituminous binder at both intermediate and high temperatures (West et al., 2013).

Evotherm is a chemical additive used as a WMA additive. The recommended additive amount is between 0.25% and 0.75% by weight of the bituminous binder (Kuang, 2012). Previous applications and laboratory studies indicated that Evotherm additive enhances the workability of the bituminous binder (Roja et al., 2018; Yu et al., 2016). Evotherm impacts the physical properties of bituminous binder. Li et al.

(2023) investigated the change in penetration and softening point values when 0.4%, 0.6%, and 0.8% Evotherm is added by weight of the binder. It was observed that as the ratio of the Evotherm increased, the penetration value increased while the softening point decreased. Therefore, the Evotherm additive softens the bituminous binder (Abdulrahman et al., 2019; Chen et al., 2023; Liang et al., 2022). Furthermore, according to the European Asphalt Association (EAPA) published in 2010, the chemical WMA additive does not affect the viscosity of the bituminous binder.

The Evotherm additive also affects the rheological characteristics of the bituminous binder. The Evotherm modification slightly reduces the high-temperature performance of the bituminous binder (Pouranian, 2020). Yu et al. (2016) examined the rheological properties of the Evotherm additive at high temperatures, revealing that the Evotherm additive increased the phase angle of the binder while reducing the $G^*/\sin\delta$ value. Hence, the Evotherm additive reduces the rutting resistance of the bituminous binder while facilitating a more viscous deformation behavior in the binder. However, the Evotherm additive enhances fatigue resistance (Liang et al., 2022). Eventually, it is reported that Evotherm does not affect the true grade or PG of the bituminous binder (Anilkumar & Awanti, 2022).

2.7.2 Comparison of Sasobit and Evotherm Additive

Evotherm and Sasobit are WMA additives; however, their effects on the bituminous binder differ. For instance, the Evotherm additive decreases the energy consumption of the bituminous binder by 50-75%, whereas the Sasobit additive reduces the energy consumption of the bituminous binder by 20% (Sharma & Kumar, 2018).

In addition, the effects of Sasobit and Evotherm on the physical and rheological characteristics exhibit variations on bituminous binders. Li et al. (2023) conducted a study of the effects of both Sasobit and Evotherm on the bituminous binder. It was revealed that Evotherm increases the penetration value and decreases the softening point, while Sasobit exhibits the opposite characteristics. Another study by Xiao et

al. (2012) compared the rheological properties of bituminous binders modified with Sasobit and Evotherm. It was observed that the phase angle value of the Sasobit-modified binder was lower than that of the Evotherm-modified binder, and the $G^*/\sin\delta$ value of the Sasobit-modified binder was higher than that of Evotherm and the base binder. Consequently, while Evotherm induces a more viscous deformation behavior in the bituminous binder, Sasobit enables a more elastic deformation behavior. Additionally, the Sasobit-modified binder exhibits a more effective rutting resistance than Evotherm. In another study (Behnood et al., 2020), the Sasobit additive was added to the bituminous binder at a rate of 3%, while the Evotherm M1 additive was added at 0.5%. It was observed that both Evotherm M1 and Sasobit additives reduced the phase angle of the bituminous binder. However, while the phase angle significantly decreased with the Sasobit-modified bituminous binder, there was a slight change observed in the case of Evotherm M1 additive. Furthermore, the Sasobit additive increased the $G^*/\sin\delta$ value, whereas the Evotherm M1 additive was observed to decrease the $G^*/\sin\delta$ value. Accordingly, the Sasobit additive enhances rutting resistance, whereas the Evotherm M1 additive reduces rutting resistance. Also, a study (Liang et al., 2022) compared the fatigue resistance of bituminous binders with added Sasobit and Evotherm additives. According to the study, while the Evotherm additive increases the binder's fatigue resistance, the Sasobit additive reduces fatigue resistance.

Considering the combined effects of Sasobit and Evotherm additives on the bituminous binder, it is evident that Sasobit contributes to the hardening of the binder, an increase in stiffness leading to improved rutting resistance, and enables the bituminous binder to display a more elastic deformation behavior. In contrast, the Evotherm additive softens the bituminous binder, decreases rutting resistance, and results in a more viscous deformation behavior.

2.8 Fourier Transform Infrared Spectroscopy (FTIR)

Due to the complexity of SARA methods, Fourier transform infrared spectroscopy (FTIR) is also utilized in recent studies to understand the chemical properties of the bituminous binders (Mirwald et al., 2020; Yao et al., 2015; Wang et al., 2019; Werkovits et al., 2022). In the molecular structure of bituminous binders, infrared radiation induces specific movements such as rotation, translation, or vibration, each tied to a distinct absorption energy and wavelength. These movements produce a distinct spectrum, resembling a molecular fingerprint within the binder (Porot et al., 2023). The interplay among functional groups within these binders is crucial, requiring precise quantification for comprehension (Peterson, 1975). Thus, FTIR stands as a characterization technique unveiling both the composition and functional groups of bituminous binders (Weigel & Stephan, 2017). Despite similar functional groups in bituminous binders sourced from different crude oil origins, their respective functional group densities slightly differ (Zojaji, 2021). Furthermore, exposure to oxidation alters the densities of functional groups in bituminous binders, eliciting varied responses based on the crude oil source (Tarsi et al., 2018). Therefore, the FTIR spectrum helps to identify specific changes in the functional groups of bituminous binders after exposure to aging, elucidating the relationship between these alterations and the rheological properties of the bituminous binder.

The aging of bituminous binders notably affects two essential chemical groups: carbonyl and sulfoxide. These alterations are highlighted in studies by Lu et al. (2008) and Petersen & Glaser (2011). Carbonyl groups indicate oxidation levels, correlating with viscosity changes during binder aging. Similarly, sulfoxide groups are crucial in understanding how bituminous binders' age. Nie et al. (2021) propose a quantitative approach, suggesting that examining the increasing presence of carbonyl and sulfoxide groups directly reflects the extent of binder aging, allowing for a quantitative determination of binder aging through these two groups. Their study of binders with various penetration values reveals distinct increments in these groups during aging. Furthermore, Koyun et al. (2020) observed alterations in

sulfoxide and carbonyl groups after long-term binder aging, whereas short-term aging showed fewer notable changes. These studies collectively emphasize the role of carbonyl and sulfoxide groups as indicators of bituminous binder aging.

In the FTIR spectrum, the area within the range of carbonyl and sulfoxide groups is calculated, not the peak height. Yang et al. (2014) explained the rationale behind calculating the concentration in the bond of carbonyl and sulfoxide groups rather than peak height. Area calculations exhibit less variation, and multiple vibrations can occur within the same band; evaluating peak heights is not particularly straightforward.

In addition to the carbonyl and sulfoxide groups, the aliphatic group, which remains unchanged with aging, is also chosen as a reference group in the analysis. The ratio of the total areas of the carbonyl and sulfoxide bond regions to the reference area of the aliphatic bond represents the aging index (AI_{FTIR}). In a recent study (Mirwald et al., 2022), the upper and lower wave numbers for carbonyl were defined as 1666-1746 cm^{-1} , for sulfoxide as 924-1066 cm^{-1} , and for aliphatic as 1319-1520 cm^{-1} . In another study (Hofko et al., 2018), the ranges used were 1660-1753 cm^{-1} for carbonyl, 970-1070 cm^{-1} for sulfoxide, and 1350-1525 cm^{-1} for aliphatic. Under short-term aging, the AI_{FTIR} shows a slight increase in bituminous binder, whereas after long-term aging, it notably increases (Hofko et al., 2017; Hofko et al., 2018; Mirwald et al., 2022). These relations are further discussed in Materials and Methods Section 3.6

CHAPTER 3

MATERIALS AND METHODS

This chapter initially explains the bituminous binders and WMA additives used in this study. Then, the physical and rheological properties of the base and modified binders are presented with respect to the standards and specifications. The weight-base SARA technique used to determine the chemical properties of the base and modified binders, which is the main purpose of the study, is explained in detail. Finally, FTIR analysis is detailed as an alternative to the SARA technique. The flow diagram of the experimental program is presented in Figure 3.1.

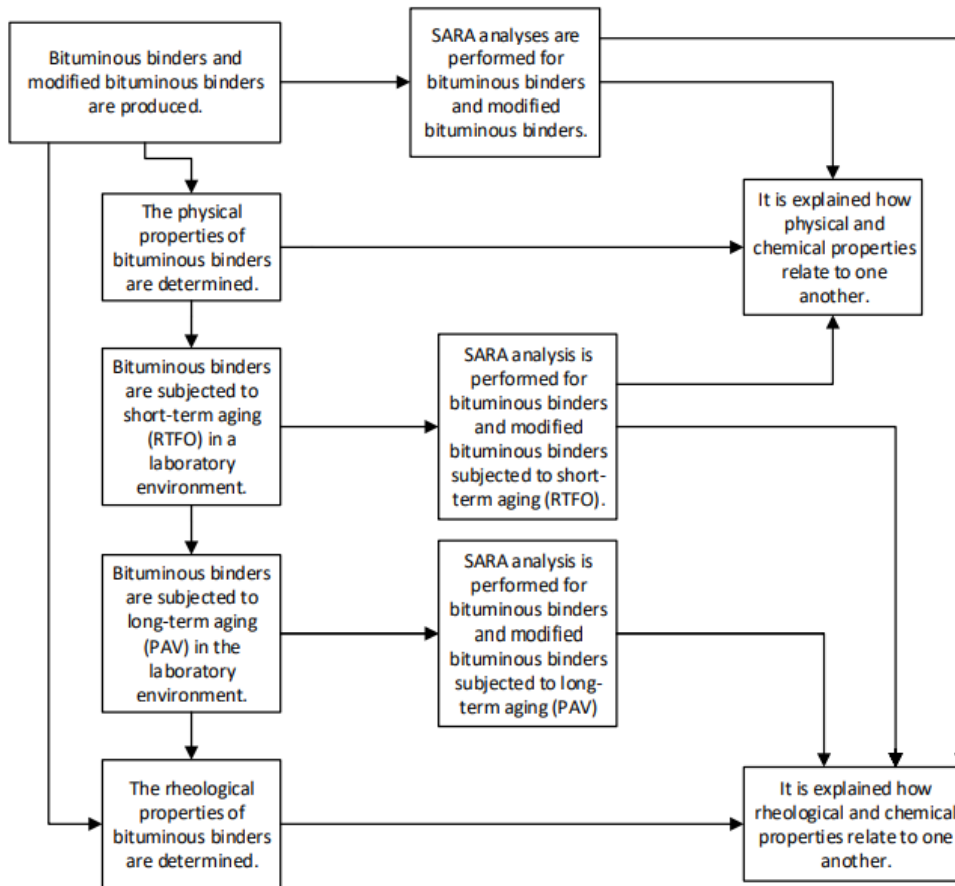


Figure 3.1. Flow diagram of the experimental program

3.1 Materials

There are six refineries in Turkey: İzmit, Batman, İzmir, Kırıkkale, Aliğa, and Star refineries, which majorly distillate imported crude oil. The Batman refinery only processes crude oil extracted from the Garzan oil fields, so the Batman refinery processes crude oil sourced domestically, whereas the other refineries in Turkey process imported crude oil. Therefore, the bituminous binders used in this study were obtained from two different refineries, Batman and Kırıkkale refinery. From both refineries, two different penetration grade binders commonly used in the road

industry (50/70 and 70/100) are obtained to analyze the differences in chemical structures and to relate these structures with physical and rheological properties. From this point on, bituminous binders are named using the first and middle letters of the refineries from which they are obtained. The 50/70 and 70/100 penetration grade binders are called BM50/70 and BM70/100 if they are supplied from the Batman refinery and KK50/70 and KK70/100 if they are provided from the Kırıkkale refinery. Additionally, within the scope of this study, 50/70 penetration grade bituminous binders obtained from both Batman and Kırıkkale refineries are modified using two different WMA additives, one organic and one chemical additive, Sasobit and Evotherm. These additives are known to alter the physical and rheological properties of the bituminous binder, as well as the chemical composition; however, the change in the chemical composition has not been quantified in earlier studies (Autelitano et al., 2017; Cao et al., 2009; Oyan & Sakib, 2022; Zhang et al., 2023). Therefore, this study implemented a comprehensive study on the base and modified bituminous binders' physical rheological and chemical properties. Consequently, the bituminous binders used in this study are summarized in Figure 3.2.

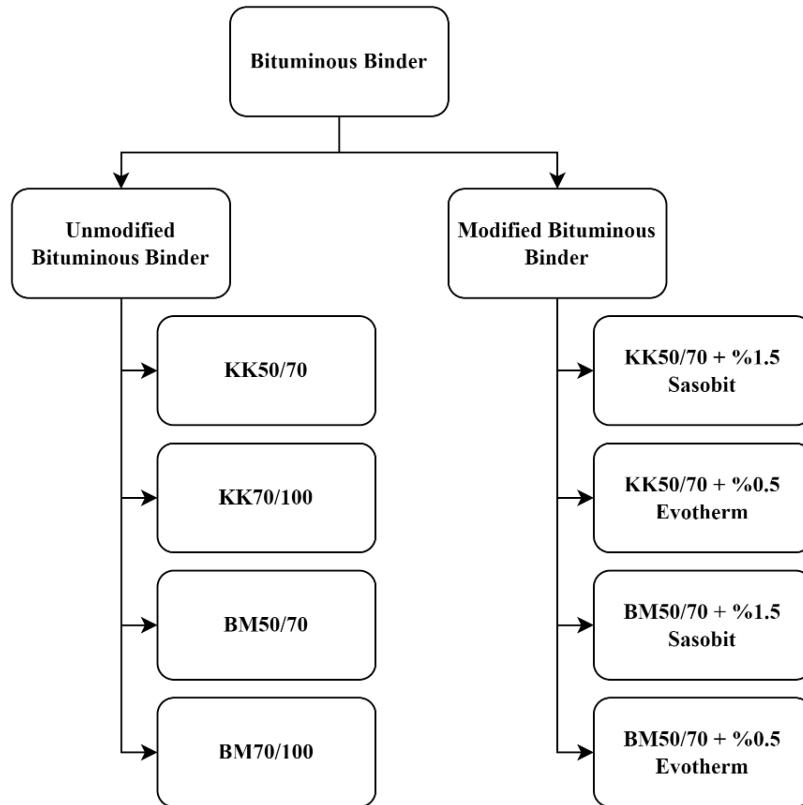


Figure 3.2. Bituminous binders used in this study

As indicated earlier, the primary objective of this study is to determine the weight-based SARA fractions of bituminous binders based on polarity. The methodology utilized in this research leads to the procedure developed by Sakib and Bhasin (2019), which will be further discussed in detail in the upcoming sections. Then, the differences in chemical fractions are reasoned and supported by numerous physical and rheological properties of base and modified bituminous binders. The physical properties of binders are determined based on penetration (ASTM D5: Standard Test Method for Penetration of Bituminous Materials), softening point (ASTM D36: Standard Test Method of Softening Point of Bitumen Ring and Ball Apparatus), flash and fire points (ASTM D92, Flash and Fire Points by Cleveland Open Cup Tester), and Brookfield viscosity tests (ASTM D4402: Standard Test Method for Viscosity

Determination of Asphalt at Elevated Temperatures Using a Rotational Viscometer). Additionally, both base and modified bituminous binders are subjected to short-term aging using the Rolling Thin Film Oven (RTFO) and long-term aging using the Pressure Aging Vessel (PAV). These experiments are performed according to ASTM D2872 (Standard Test Method for the Effect of Heat and Air on a Moving Film of Asphalt) and ASTM D6521 (Standard Practice for Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel), respectively. To characterize the rheological properties of the binders exposed to short-term and long-term aging, the Dynamic Shear Rheometer (DSR) test is also performed by ASTM D7175-15 (Standard Test Method for Determining the Rheological Properties of Asphalt Binder Using a Dynamic Shear Rheometer). The details of the experiments are also given in the following sections.

3.2 Preparation of Modified Binders with WMA additives

Bituminous binders from the 50/70 penetration grade, obtained from the Batman and Kırıkkale refineries, are modified using two different WMA additives, Sasobit and Evotherm. The addition of Sasobit, an organic additive, affects the physical properties of the bituminous binder and enhances its rheological properties, resulting in improved performance, such as better rutting resistance. Sasobit is also known to decrease the binder's viscosity (Julaganti et al., 2017; Li et al., 2021). The color of the Sasobit is pale brown, and the physical state is solid (Behnood et al., 2020). It is recommended to be added between 0.8% and 3% by weight of the bituminous binder (Hurley & Prowell, 2005). The other additive used in the study is Evotherm M1, a chemical additive that decreases viscosity while influencing the physical and rheological properties of the bituminous binder. However, its efficacy at high temperatures is not as pronounced as Sasobit. The physical status of Evotherm M1 is liquid, and its color is amber-brown (Behnood et al., 2020). The recommended additive amount is between 0.25% and 0.75% by weight of the bituminous binder (Kuang, 2012).

In this study, the additive rates used are selected following the recommendations from the manufacturers and according to the practice in the literature. Therefore, Sasobit and Evotherm are added at a rate of 1.5% and 0.5% by weight of the binder, respectively. For the modification process, bituminous binders are initially heated to 130 °C for about 40 minutes until they reach a fluid consistency. Then, a designated weight of the bituminous binder is transferred to an empty flask, and a specified amount of additive is added. Immediately after transferring the bituminous binder and additive to the flask, the flask is placed on the hot plate in the range of 125-133°C. When the constituents in the flask reach the same temperature range, the mechanical (end-over-end) mixer tip is immersed into the flask, and the mixing process is initiated. For all modified binder preparations, the process, a 10-minute mixing duration at a 1200 rpm mixing rate, is kept constant.

3.3 Bituminous Binders Physical Characteristics

Bituminous binders in Turkey are classified into penetration grades based on the Technical Specification for Highways (KGM, 2013). The properties of bituminous binders with penetration grades 50/70 and 70/100 should be compatible with those shown in Table 3.1 to be used in road construction. Table 3.2 presents the physical characteristics of binders obtained from the two different refineries owing to two different penetration grades in this study. The penetration values of KK50/70 and BM50/70 binders are determined as 48 and 45, respectively. These values do not comply with the bituminous binder classification standards, given in Table 3.1. Since the penetration values of the binders are close to the lower bound of the specification limits and compatible with their softening points, binders are still classified in the 50/70 class. Moreover, the physical properties of KK70/100 and BM70/100 binders comply with the specifications.

It should also be highlighted that the differences in the physical properties of the same penetration grade binders depend on the refinery process and crude oil source. It is observed that the bituminous binders obtained from the Kırıkkale refinery

exhibit higher penetration but lower softening points than bituminous binders obtained from the Batman refinery. It can be concluded that the binders collected from the Batman refinery are harder than those obtained from the Kırıkkale refinery.

Table 3.1 Bituminous binder standard (KGM, 2013)

Property	Standard	Bituminous Binder Class	
		B50/70	B70/100
Penetration Test (25C°) 0.1 mm	TS EN 1426	50-70	70-100
Softening Point (C°)	TS EN 1427	46-54	43-51
Loss on Heating (%)	TS EN 12607-1	≤0.5	≤0.8
Flash Point (C°)	TS EN ISO 2592	≥230	≥230

Table 3.2 Physical properties of base bituminous binders

Property	Standard	Unit	KK50/70	KK70/100	BM50/70	BM70/100
Penetration (25 °C)	ASTM D5	0.1 mm	48	77	45	73
Softening Point	ASTM D36	°C	52.5	50	54	51.5
Flash Point	ASTM D92	°C	308	290	278	256
Fire Point	ASTM D92	°C	352	344	302	290

Depending on the refinery that the base binders provided, modified bituminous binders also undergo some changes in their physical properties. Table 3.3 and Table 3.4 presents the changes in the physical characteristics of binders sourced from the Kırıkkale and Batman refineries after modification with Sasobit and Evotherm, respectively. It is observed that adding Sasobit at a rate of 1.5% decreases the penetration and increases the softening point. On the contrary, adding Evotherm at a rate of 0.5% increases the penetration value and decreases the softening point. These statements also meet the findings of Li et al. (2023).

Table 3.3 The physical properties of modified bituminous binders obtained from Kırıkkale refinery

Property	Standard	Unit	KK50/70	KK50/70	KK50/70
				+ %1.5 Sasobit	+ %0.5 Evotherm
Penetration (25 °C)	ASTM D5	0.1 mm	48	44	52
Softening Point	ASTM D36	°C	52.5	55.5	50.5
Flash Point	ASTM D92	°C	308	300	280
Fire Point	ASTM D92	°C	352	340	332

Table 3.4 The physical properties of modified bituminous binders obtained from Batman refinery

Property	Standard	Unit	BM50/70	BM50/70	BM50/70
				+ %1.5 Sasobit	+ %0.5 Evotherm
Penetration (25 °C)	ASTM D5	0.1 mm	45	42	53
Softening Point	ASTM D36	°C	54	59.5	52
Flash Point	ASTM D92	°C	278	258	235
Fire Point	ASTM D92	°C	302	300	277

The viscosity tests of base and modified binders are performed following ASTM D4402: Viscosity Determination of Asphalt at Elevated Temperatures Using a Rotational Viscometer. Using Brookfield RVDV-II PRO. The viscosities are measured at intervals of 10 °C within the temperature range of 120 °C to 180 °C. Within the procedure, 10±0.5 grams of binder is preheated to a pourable consistency

before being poured. Simultaneously, the 27# spindle and metal container intended for the experiment are also subjected to heating. Once the heating chamber reaches 110°C, the bituminous binder is introduced into the metal container. Subsequently, the container is placed in the device, and following the addition of the preheated spindle, then the program is initiated. At each temperature, the spindle rotates at a specific speed, and six sets of data are obtained in centipoise. The average of these six numbers provides the viscosity of the bituminous binder at that temperature. The experiment duration is approximately 5 hours per sample. After the experiment, the viscosity-temperature curves are obtained, and will be further presented and discussed in Result and Discussions.

3.4 Rheological Properties of Bituminous Binders

The rheological properties of bituminous binders are as important as their physical properties. Thus, these properties are examined to consider their behavior under short-term or long-term aging. According to the ASTM D2872 standard (Standard Test Method for Effect of Heat and Air on a Moving Film of Asphalt Binder), the Rolling Thin Film Oven (RTFO) test is used to subject the bituminous binders to short-term aging. During the RTFO test, the bituminous binders are exposed to heat and airflow. Eight glass containers with a height of 140 mm and a domed mouth opening featuring a radius of 32 mm are used for sampling per test. Each container is filled with 35 ± 0.5 grams of bituminous binder. Over 85 minutes, the air is freely sprayed into the rotating containers at a rate of 4000 ± 200 ml/min, maintaining a temperature of 163 ± 0.5 °C. In advance and at the termination of the experiment, mass determinations are carried out on the samples to ascertain the extent of reduction, thereby quantifying the amount lost material during the process. The amount and percent of mass loss in bituminous binders are given in Table 3.5. According to the technical specifications of the General Directorate of Highways in Turkey, the permissible percentage loss for the 50/70 and 70/100 penetration grades are less than or equal to 0.5% and 0.8%, respectively (See Table 3.1). The results obtained from

the bituminous binder used in this study comply with the specification limits. Moreover, it can be concluded that regardless of the WMA additive used, the volatile substances increase with the addition of the WMA additives.

Table 3.5 Mass loss of base and modified binders

Bituminous Binders	Mass Loss (gr)	Mass Loss (%)
KK50/70	0.06	0.16
KK70/100	0.08	0.24
BM50/70	0.10	0.29
BM70/100	0.16	0.47
KK50/70 + %1.5 Sasobit	0.09	0.26
BM50/70 + %1.5 Sasobit	0.11	0.30
KK50/70 + %0.5 Evotherm	0.17	0.49
BM50/70 + %0.5 Evotherm	0.18	0.52

The long-term aging process is carried out using a Pressure Aging Vessel (PAV) following ASTM D6521: Standard Practice for Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel. Bituminous binders, exposed to short-term aging with RTFO, are poured into metal PAV pans in quantities of approximately 50 ± 0.5 grams. The diameter of the PAV pan is 140 mm, and its height is 9.5 mm. After the samples are prepared, the vessel and a pan holder are brought to a constant temperature of 100°C. At the end of this stabilizing period, the vessel's lid is opened, and the pan holder is quickly placed into the chamber, followed by the closure of the lid. Due to the lid opening, there is a sudden temperature drop, so placing the pan holder as quickly as possible is essential to minimize the temperature difference. Once the vessel's temperature is stabilized back to 100°C, a pressure of 2.1 MPa is applied, and the samples are exposed to both a temperature of 100°C and a pressure of 2.1 MPa for 20 hours. After the elapsed time, the pressure is released slowly within at least 15 minutes, and the samples are removed from the vessel. The samples are then heated in a 165°C oven for about 15 minutes, poured into a metal container with a radius of 38.3 mm and a depth of 50 mm, then placed in a vacuum oven. In this

step, the air inside the samples is extracted with the help of a vacuum. Following a 15-minute preheating at 170°C, a pressure of 15 kPa is applied for 30 minutes. As a result of the procedures, the bituminous binders are ready to be analyzed after exposure to long-term aging. Dynamic Shear Rheometer (DSR) test is used to investigate the changes in rheological properties of the unaged and aged bituminous binders subjected to short-term and long-term aging. The DSR test, performed according to ASTM D7175 (Standard Test Method for Determining the Rheological Properties of Asphalt Binder Using a Dynamic Shear Rheometer), is run using the Malvern Kinexus KNX2210 device. The complex shear modulus (G^*) and phase angle (δ) obtained from the DSR are crucial in examining bituminous binders' rheological properties. The complex shear modulus assists in understanding the binder's resistance to deformation, while the phase angle is crucial in determining whether the bituminous binder exhibits viscous or elastic behavior. At a phase angle of 90°, the bituminous binder exclusively exhibits viscous deformation behavior, while a phase angle of 0° signifies elastic deformation behavior. In the DSR, different plate geometries are used to evaluate these parameters.

A 25 mm plate geometry is used for the unaged and aged bituminous binders subjected to short-term aging (RTFO). For the long-term aged (PAV) bituminous binders, an 8 mm plate geometry is used. For the 25 mm plate geometry, the gap value is 1 mm, while for the 8 mm plate geometry, it is 2 mm. The liquified bituminous binder is poured into the silicone molds in the desired diameter and thickness. After the bituminous binder has cooled to room temperature, it is placed between the two plates, and excess bitumen is trimmed. To determine the true grades of the bituminous binders, the Rfinder tool coupled with DSR equipment is used. According to AASHTO M320, for unaged bituminous binders, $G^*/\sin(\delta)$ should be ≥ 1.0 kPa; for bituminous binders subjected to RTFO aging, $G^*/\sin(\delta)$ should be ≥ 2.2 kPa, and for bituminous binders subjected to PAV aging, $G^*\sin(\delta)$ should be ≤ 5000 kPa. The minimum temperature value that satisfies the specified condition is the true grade of the bituminous binder. After determining the true grade, a frequency sweep test is performed on the bituminous binders. In this test, the temperature of

the bituminous binder is increased in increments at a rate of 6°C within the range of 34°C to 76°C. Twenty-one frequency levels, ranging from 0.1 Hz to 10 Hz, are employed throughout the test. Consequently, the rheological properties of the bituminous binders, including complex shear modulus and phase angle, are determined through the DSR test at high (unaged and RTFO binder) and intermediate (PAV binder) temperatures.

DSR measurements is used to construct master curves incorporating complex shear modulus and phase angle. This approach facilitates a more comprehensive interpretation of the data and discerns differences among the various bituminous binders. In this study, the sigmoidal model developed within the National Cooperative Highway Research Program (NCHRP) Project A-37A is used to develop the master curves using Eq. (1) and (2) (Pellinen et al., 2004).

$$f_R = f a(T) \quad \text{or} \quad \log(f_R) = \log(f) + \log(a(T)) \quad (1)$$

Where f and f_R are frequency and reduced frequency (Hz), respectively. T is the test temperature (°C). $a(T)$ is the shift factor. At the reference temperature ($T=64^\circ\text{C}$ for this study), $a(T)$ is equated to 1.

$$\log|E^*| = \delta + \frac{\alpha}{1 + e^{\beta - \gamma(\log f_R)}} \quad (2)$$

$$\log|E^*| = \delta + \frac{\alpha}{1 + e^{\beta - \gamma(\log f_R)}} \quad (3)$$

Where δ is the minimum complex shear modulus, α indicates the difference between maximum and minimum complex shear modulus. β and γ are the shape parameters. Once the master curve is built binder, it aids in assessing the rutting or fatigue behavior of bituminous binders across a wide range of frequencies and temperatures.

3.5 Experimental Study of weight-based SARA Simplified Technique

In this study, the methodology proposed by Sakib and Bhasin (2019), titled "Test Method for Separation of Bitumen into Four Fractions Using Pre-packaged Cartridges," is used to fractionate bituminous binders into saturate, aromatic, resin, and asphaltene (SARA) components based on polarity. According to this methodology, the asphaltene and maltene fractions were initially separated using the insolubility property of the asphaltene fraction. Then, the maltene fractions were separated through chromatography-based fractionation utilizing pre-packaged columns. The development of the procedure was inspired by ASTM D4124 (Standard Test Method for Separation of Asphalt into Four Fractions) and IP469 standard (Determination of saturate, aromatic, and polar compounds in petroleum products by thin layer chromatography and flame ionization detection). In this study, the SARA analysis was performed on 24 different bituminous binders (4 base binder at 3 different aging levels + 4 modified binder (2 base binder * 2 WMA additive) at 3 different aging levels). Since three replicates were performed per each binder, overall, 72 SARA analyses were eventually carried out. The details related to test setup and procedures are given in the following sections.

3.5.1 Details of Test Setup

The setup of the weight-based SARA method consists of several components. Therefore, this section discusses these components, and their features as follows:

- Balance: The balance with a precision of 0.001 g.
- Wide-Mouth Glass Bottle: The wide-mouth glass bottle with a capacity of 80 ml.
- Magnetic Stirrer: The magnetic stirrer with speed and temperature adjustments, necessary during winter conditions when room temperature is lower than 20 °C.

- 22 Gauge Needle: 22G x 0.7x150 mm spinal needle
- PTFE Filters: The PTFE filters with a pore size of 0.2-0.22 μm and 25-30 mm diameter.
- Solid Phase Extraction (SPE) Cartridge: SPE cartridges with a capacity of 20 ml and contain 5 g of silica gel.
- Vials: The vials are made of glass and have a capacity of 40 mL with a diameter of 27.5 mm and a length of 97 mm.
- Syringes: Syringes with a capacity of 80 ml and 10 ml each are used.
- Vacuum Manifold: Any type or capacity of vacuum manifold suitable for a regular-size syringe tip is sufficient for the operation. The vacuum manifold used in this study is the Supelco Visiprep™ SPE Vacuum Manifold 12-port model.
- Vacuum pump: The vacuum pump is connected to the vacuum manifold. In this study, a two-stage vacuum pump (VE225) was utilized, and the ultimate vacuum of the vacuum pump is 3×10^{-1} Pa.
- Oven: To dry the PTFE filters.
- Nitrogen Purging Oven: Oven capable of evaporating the solvents at a specific vacuum setting (3 mbar) and temperature (135°C) and collecting in a solvent trap.

3.5.2 Details of the Solvents

Solvents used in the SARA analysis are discussed in this section. These reagents help separate the polar-based fractions of the bitumen binder. As indicated in the ASTM D4124 standard and Sakib and Bhasin procedure, it is recommended to use HPLC-grade chemicals to determine the fractions, as presented in Table 3.6.

Table 3.6 Solvents used for separation of maltene into S-A-R fractions

Solvents	Quantity	Collected Fraction
N-heptane	20 ml	Prewash
Maltene + n-heptane	15 + 10 ml	Saturate
Toluene + n-heptane (80:20)	25 ml	Aromatic
DCM + Methanol (90:10)	30 ml	Resin

3.5.3 Preparation Stage of Bituminous Binder

Bituminous binders are known to be in solid form at room temperature. To separate bituminous binders into their chemical fractions, they must be initially dissolved with a reagent. This section will explain the preparation of bituminous binders before asphaltene-maltene separation. Initially, the bituminous binder should be heated with care without overheating or exposing it to aging during the heating process in the oven; in fact, it should never be heated above 50°C of its predicted softening point. When the bituminous binder becomes fluid, it can be easily poured into a silicone mold up to 400 ± 20 mg or scooped using a metal spoon. The weight of the bitumen should be recorded as M_{binder} . After pouring the bituminous binder, it is placed into a wide-mouthed glass bottle and mixed with n-heptane. For 400 ± 20 mg of bituminous binder, 40 mL of n-heptane is used to dissolve the bituminous binder. A magnetic stirrer is used for the mixing process. The stirrer also has a temperature control. During the experiments, it was noticed that when the ambient temperature was low in the laboratory during wintertime, the bituminous binder did not completely dissolve in n-heptane. Therefore, the heating function of the magnetic stirrer was used in experiments conducted during the winter season, when necessary. After adding the bituminous binder, the mouth of the glass bottle is quickly sealed since n-heptane is a solvent that rapidly evaporates. In addition, n-heptane can also evaporate upon contact with air, the air inside the glass bottle is withdrawn using a

syringe by opening a tiny hole on the bottle cap and quickly sealed back by a tape. The amount of air to be withdrawn should be 1.25 times the remaining volume after filling 40 mL of n-heptane. The mixing speed of the magnetic stirrer is set to 200 rpm, and if necessary, the temperature is adjusted to approximately 25°C. The mixing duration is 24 ± 2 hours.



Figure 3.3. The Stirring process of bituminous binder and n-heptane

3.5.4 Separation of Bituminous Binder into Two Fractions: Asphaltene and Maltene

Asphaltene and maltene are the two main fractions of bituminous binder based on their polarity property. After stirring the bituminous binder in n-heptane for 24 ± 2 hours, the solution becomes suitable for separation into asphaltene and maltene fractions. For this separation, four numbered and pre-weighed vials are prepared. The prepared vials are sequentially placed into the vacuum manifold. Additionally, four clean PTFE filters with known weights are prepared, numbered, and placed onto

the appropriate port of the vacuum manifold, aligning with the numbered vials. 10 ml syringes without pluggers are placed on the PTFE filters (Figure 3.4 a). Using a syringe, 10 ml of the solution of binder and n-heptane is taken and poured into each syringe placed on the PTFE filters. Initially, the port of the vacuum manifold is opened by turning it, and after the flow starts into the vial, the vacuum is activated. The drip rate is kept constant around 3-4 drops per second. There is no specific configuration for the vacuum rate; in fact, what demands more attention than the vacuum setting is the drip rate. An excessive drip rate may result in the solution splashing; hence, the drip rate requires attention at this stage. The solution first passes through the PTFE filters and then begins to flow into the vial. As known, the asphaltene fraction is a polar fraction insoluble in n-heptane. Therefore, asphaltene cannot pass through the PTFE filter's 0.2-0.22 μm pore; they remain inside the filter while the maltene fraction collects in the vials (Figure 3.4 b). When the dripping of the 10 mL solution into the vials is almost complete, an additional 5 mL of n-heptane is added to obtain the remaining maltene. At this stage, asphaltene particles may accumulate at the bottom of the syringes without a plugger; to prevent this, syringes that have no plugger are gently agitated by hand. After the extra n-heptane has been fully transferred into the vial, the vacuum is left for a very short period. This allows the remaining n-heptane within the PTFE filter to drip into the vial completely. Once the dripping ends, the vacuum is closed, and the separation process is complete. This process is carried out four times for all binder and n-heptane solutions.

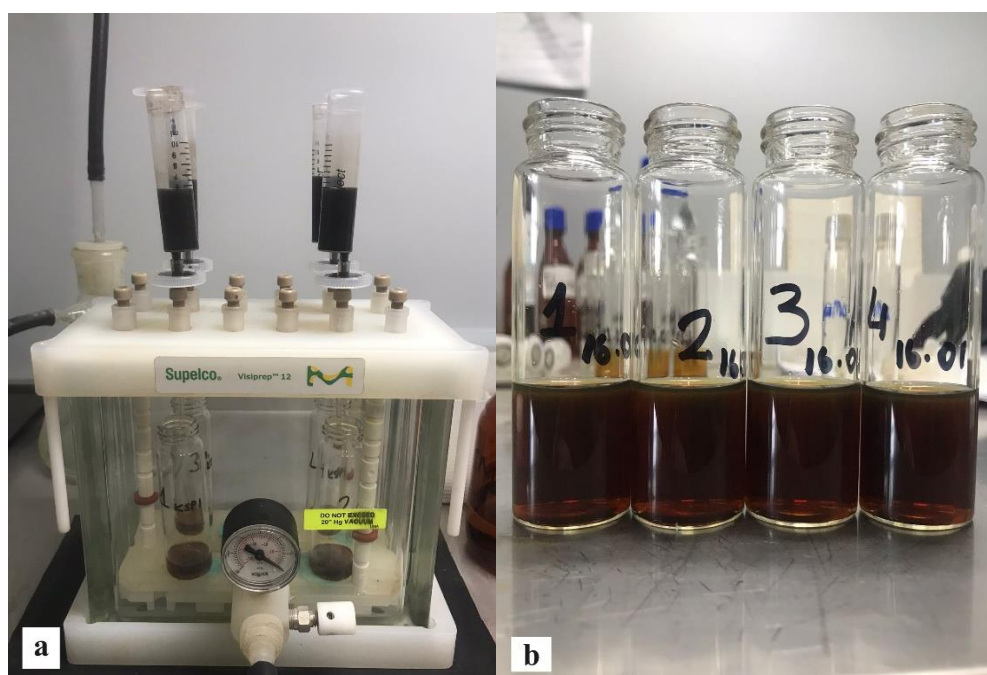


Figure 3.4. a) Asphaltene-Maltene separation b) Maltene-n-heptane solutions

3.5.5 Drying Process of Asphaltenes and Maltenes

After the separation process, the maltene fraction is collected in four equal vials containing 15 ml of maltene solution (Figure 3.4). Two of these vials are selected and placed in a nitrogen-purged oven and dried at 120 °C for 45 minutes (Figure 3.5). Once the drying process is complete, the vials are weighed on a precision balance with a sensitivity of 0.001 grams to determine amount of maltene in each vial.

In the second part of the SARA analysis, maltene is used in a specific amount to separate into saturate, aromatic, and resin fractions. The amount of maltene used is determined according to the procedure introduced by Sakib and Bhasin, which should be 50 mg maltene in 15 ml of solution, equivalent to the maltene density of 3.33 mg/ml. A proportional relationship is used to adjust this density based on the amount of maltene in the vials dried in a nitrogen-purged oven, and accordingly, the amount of extra n-heptane to be added is determined. The extra n-heptane solutions

are added to the non-dried two vials. To verify the density adjustment, a pre-weighed clean vial is used, and 15 mL of the adjusted solution is added to this vial using a syringe, and then dried at 120 °C for 45 minutes. After drying, the change in the vial weight should be 50 ± 2 mg. Once the verification is completed, the solution in the other vial is used to separate the maltene fraction into saturate, aromatic, and resin fractions. The following section will explain this process extensively, where maltene is fractionated into S-A-R components.

During the separation of asphaltene-maltene, the solution passes through PTFE filters, causing the filters to become moist. N-heptane is a highly volatile organic compound, and the moisture is expected to evaporate in a few hours. However, a few hours of drying time are insufficient due to the small pore size of PTFE filters. Based on experiments, it has been observed that the filters do not completely dry even after waiting for a week at room temperature. Therefore, it is necessary to place the PTFE filters in an oven for drying. The experiments showed that the structure of PTFE filters is compromised at around 150 °C, so it is crucial to dry the filters in the oven without damaging their structure. In this study, the PTFE filters are dried in a 120 °C oven for 2 hours. After drying, the amount of asphaltene in the filters is determined (Figure 3.6). The sum of the asphaltene content in the four PTFE filters gives the total asphaltene weight in the bituminous binder and is recorded as $M_{\text{asphaltene}}$.

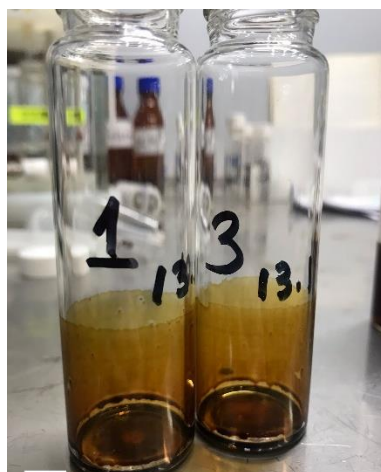


Figure 3.5. Dried maltene vials



Figure 3.6. Clean and used PTFE filters

3.5.6 Separation of Maltene into Three Fractions: Saturate, Aromatic and Resin

This section will elucidate the process of fractionating saturate, aromatic, and resin components from the maltene solution. The separation procedure employs specific solvents, pre-packaged cartridges (SPE), and vacuum techniques. Initially, the saturate fraction is separated, followed by the aromatic fraction, and ultimately, the resin fraction is separated.

Initially, four clean vials with known weights are prepared for the separation process, each designated for pre-washing, saturate, aromatic, and resin fractions, respectively. These vials are sequentially placed into the vacuum manifold. After ensuring that all ports of the vacuum manifold are closed, the SPE cartridges are securely positioned onto the port above the pre-washing vial. 20 ml of n-heptane is transferred into the SPE cartridge with a syringe, allowing the solvent to pass through the column to the vial (Figure 3.7). Once dripping begins, the vacuum is initiated. Since the flow rate is more critical than the vacuum level, the vacuum is adjusted to achieve a rate of 3-4 drops per second. Excessive vacuum may lead to solution spraying, resulting in sample loss. After the dripping is completed, the mouth of the SPE cartridge is manually closed, permitting the occurrence of a few last drops. Once the dripping ceases, the vacuum is turned off, followed by closing the port, and the pre-washing process is complete.



Figure 3.7. Process of pre-washing of SPE cartridge with 20 ml n-heptane

In the next step, the saturate fraction is separated. For this purpose, the SPE cartridge is removed onto the port above the saturate vial. A maltene solution with a 3.33 mg/mL density is added to the SPE cartridge, and the port is opened. The maltene solution within the SPE cartridge is allowed to drip into the vial (Figure 3.8 a), and once dripping commences, the vacuum is activated. The vacuum settings from the pre-washing stage apply to this phase as well. The drop speed is adjusted to 3-4 drops per second. After dripping ceases, the vacuum is turned off first, and then a 10 mL n-heptane solution is added to the SPE cartridge (Figure 3.8 b), reactivating the vacuum. Once dripping stops, the mouth of the SPE cartridge is manually closed, like the pre-washing stage, and it has waited until dripping comes to a complete stop. When dripping has ceased, the vacuum is turned off first, followed by closing the port, and the saturate fraction is separated in the maltene solution.

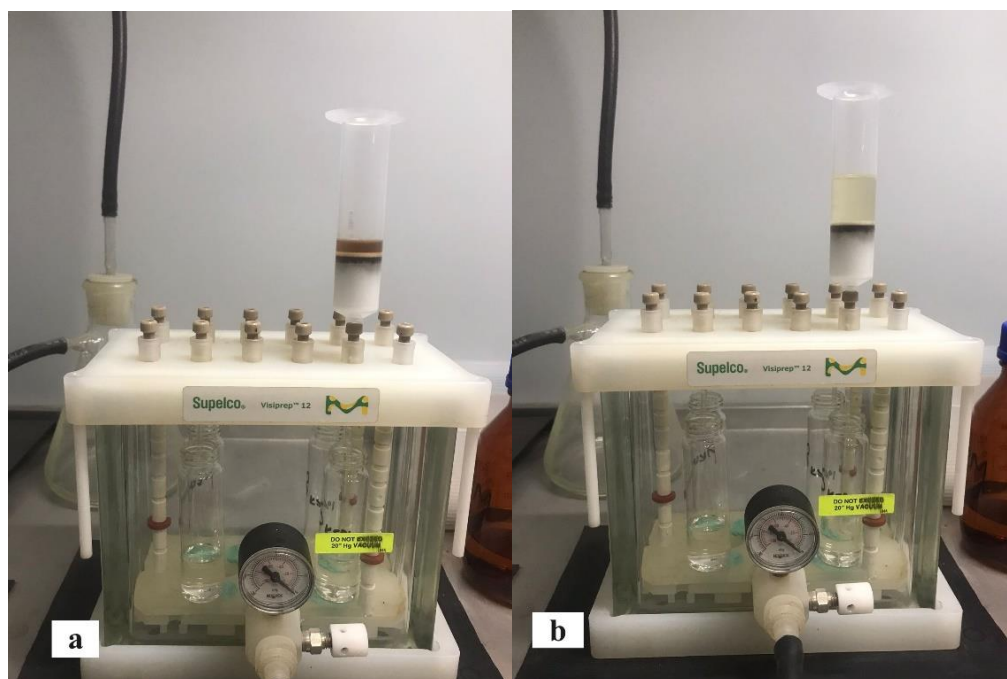


Figure 3.8. 15 ml Maltene solution poured into SPE cartridge b) 10 ml n-heptane added after Maltene separation for cleaning

Then, the SPE cartridge is moved to the port corresponding to the aromatic vial to separate the aromatic fraction. An 80:20 mixture of toluene and n-heptane is used to separate the aromatic fraction. For this purpose, 20 mL of toluene and 5 mL of n-heptane solution is poured into the SPE cartridge. The steps for pre-washing and separating the saturate fraction are repeated, and once the dripping stops, the aromatic fraction is collected in the vial.



Figure 3.9. Toluene: n-heptane poured into SPE cartridge

After separating the aromatic fraction, the SPE cartridge is finally placed on the port corresponding to the resin vial to separate the resin fraction. A 90:10 mixture of Dichloromethane (DCM) and Methanol solution separates the resin fraction. For this study, the preferred amounts are 27 mL of DCM and 3 mL of methanol solution. The solvent mixture is added to the SPE cartridge (Figure 3.10), and the extraction steps are repeated. However, after the dripping stops, the vacuum can ultimately be increased to draw the sample inside the SPE cartridge, and the resin fraction is collected in a vial.



Figure 3.10. DCM: Methanol poured into SPE cartridge

It is crucial to perform these steps with great care to prevent any material loss, and it is essential to consider that the solvents used are volatile. The saturate, aromatic, and resin fractions in the 50 ± 2 mg maltene fraction are separated at the end of this separation process (Figure 3.11).

The vials are individually dried in a nitrogen-purged oven. It is recommended to dry the S-A-R vials for 15 minutes at 125°C , 15 minutes at 130°C , and 60 minutes at 135°C (Sakib & Bhasin, 2019). However, it was observed during the study that the recommended duration was insufficient for complete drying. Additionally, due to the inability to adjust the nitrogen-purged oven as recommended, the vials were dried at 135°C for 100 minutes in this study. After drying, the vials with known empty weights are weighed on a balance with a sensitivity of 0.001 grams, and the weights of the saturate (M_{saturate}), aromatic (M_{aromatic}), and resin (M_{resin}) fractions in the vials are determined.



Figure 3.11. S-A-R fractions

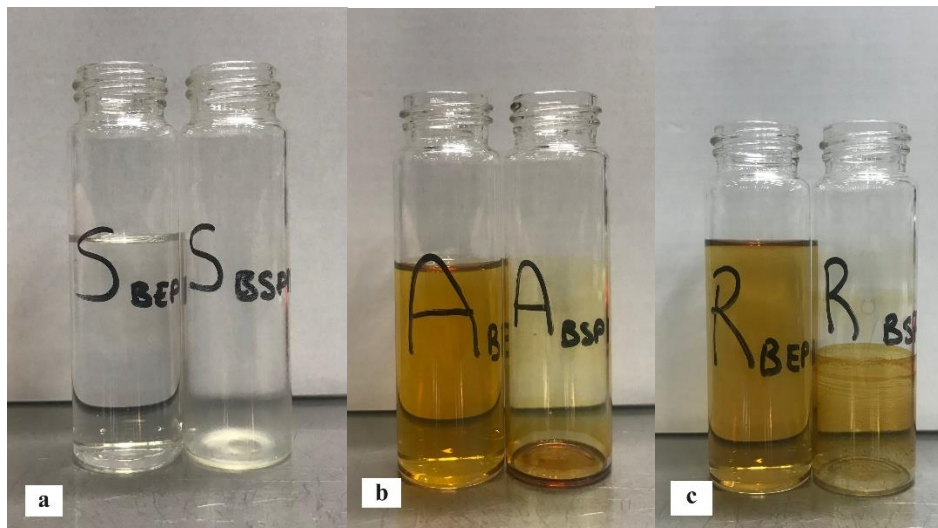


Figure 3.12. a) Saturate fraction before and after drying b) Aromatic fraction before and after drying c) Resin fraction before and after drying

3.5.7 Calculation of SARA Fractions

The determination of the percentage of SARA fractions within the bituminous binder is calculated using the initial binder weight (M_{binder}) and fractions weights ($M_{\text{asphaltene}}$, M_{maltene} , M_{saturate} , M_{resin} , $M_{\text{aromatics}}$). The determination of each fraction weight is discussed in the earlier sections. From Eq. (4) to Eq. (9), the percentage calculations are presented in a sequence.

$$Asphaltene (\%) = \frac{M_{asphaltene}}{M_{Binder}} \quad (4)$$

$$Maltene (\%) = 100\% - Asphaltene\% = \frac{M_{Maltene}}{M_{Binder}} \quad (5)$$

Check Calculation:

$$M_{maltane-15ml} = (1 \pm 0.02) * (M_{saturate} + M_{aromatics} + M_{resins}) \quad (6)$$

$$Saturate (\%) = \frac{M_{saturate}}{M_{maltane-15ml}} * \frac{\%Maltene}{100} \quad (7)$$

$$Aromatic (\%) = \frac{M_{aromatics}}{M_{maltane-15ml}} * \frac{\%Maltene}{100} \quad (8)$$

$$Resin (\%) = \frac{M_{resins}}{M_{maltane-15ml}} * \frac{\%Maltene}{100} \quad (9)$$

3.5.8 Gaestel Index (Ic)

To comprehend the difference in the rheological properties of bituminous binders, researchers examine the colloidal structure of bituminous binders. Bituminous binders are considered to have a colloidal system. This system examines the dispersed or dissolved state of asphaltene micelles within the maltene. Resins, consisting of a stabilizing and solvent layer, and asphaltenes form the micelles. The colloidal structure of bituminous binders comprises two types of sol and gel. Sol type demonstrates Newtonian behavior, meaning that with sufficient solvent power from resins and aromatics, asphaltenes become fully peptized, resulting in well mobility of the resulting micelles. Gel-type bituminous binders, on the other hand, exhibit non-Newtonian behavior. In the gel type, micelles have an irregular and mixed structure due to their inability to peptize because of insufficient aromatic/resin content. (Hunter et. al., 2015; Lesueur, 2009; Weigel & Stephan, 2018). The Gaestel Index (Ic) is used to understand the colloidal structure in the composition of bituminous binders (Gaestel et al., 1971). According to Eq. (10), the sum of

asphaltene and saturate fractions is divided by the sum of aromatic and resin fractions.

$$I_c = \frac{\text{Asphaltene (\%)} + \text{Saturate (\%)}}{\text{Aromatic (\%)} + \text{Resin (\%)}} \quad (10)$$

The Gaestel Index of a bituminous binder typically ranges between 0.5 and 2.7. A bituminous binder displays sol-type behavior when I_c is greater than 0.5, while for a gel-type behavior, I_c is typically below 0.22 (Gaestel et al., 1971; Paliukaite et al., 2014; Paliukaite et al., 2015). According to studies in the literature, the I_c value obtained from SARA fractions of bituminous binders increases with aging, which is also related to a dramatic increase in the asphaltene fraction with the binder aging (Kleizienė et al., 2019; Siddiqui & Ali, 1999). As the asphaltene fraction rises, the increasing I_c value leads to the asphaltene micelles of the binder being found dispersed within the maltene, resulting in gel-type behavior along with the increase in the asphaltene fraction of the bituminous binder. Moreover, as the I_c value increases, it implies a decrease in the stability of the binder (Camargo et al., 2020; Oliver, 2012). In this study, the Gaestel Index values are calculated for all base and modified bituminous binders to establish a relationship with the characteristics of the bituminous binders.

3.6 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR), which helps to identify the functional groups of bituminous binders, has also been used in this study to understand the chemical properties of bituminous binders. The FTIR analyses conducted in this study were performed using Bruker Alpha Platinum ATR (Attenuated Total Internal Reflectance) instrument and Opus 7.8 software (See Figure 3.13).

For the sample preparation, the bituminous binders are initially heated at 160°C for about half an hour. Once the bituminous binder becomes liquid, it is thoroughly

mixed with a clean glass rod, since the homogeneity of the samples are crucial for the procedure. A drop of each binder with 1 mm thickness is taken for the analysis. The sample droplet at room temperature is carefully placed onto the equipment sensor. Within approximately 1 minute, the spectra of the bituminous binder are obtained. ATR spectra are obtained from the wavenumber range between 4000 and 500 cm^{-1} with a resolution of 4 cm^{-1} for each binder. The spectra of bituminous binders are then transferred to OriginProLab Software. A min-max normalization is applied to the spectrum to reduce errors that could arise from the crystal of ATR. After this normalization stage, three functional groups are analyzed to determine the aging index of the bituminous binder. The first one is the Carbonyls group (CO) within the range of 1660-1800 cm^{-1} , the second one is Sulfoxides (SO) within the range of 1079-984 cm^{-1} , and the third is the range of 1525-1350 cm^{-1} , attributed to the Aliphatic band (CH₃) (Mirwald, et al., 2022). Using OriginProLab Software, areas within the range of carbonyl groups (A_{CO}), sulfoxides (A_{SO}), and the aliphatic band (A_{CH₃}) are determined by integration. The integrated areas are used to calculate the Aging Index of the bituminous binder (A_{FTIR}), as given in Eq. (11).

$$A_{FTIR} = \frac{A_{CO} + A_{SO}}{A_{CH_3}} \quad (11)$$

In this study, FTIR analysis was conducted on a total of 24 different bituminous binders (4 base binders at 3 different aging levels + 4 modified binders (2 base binders * 2 WMA additive) at 3 different aging levels). For each binder, this analysis is repeated for three replicates of each binder to ensure the quality of the data.



Figure 3.13. ATR-FTIR Analysis instrument

CHAPTER 4

DISCUSSION AND RESULTS

In this chapter, a comprehensive analysis is conducted to quantify and discuss the influence of SARA fractions on the physical and rheological properties of modified and unmodified binders, considering the aging effect. Moreover, these relationships and findings are also supported by the functional groups determined by the FTIR analysis.

4.1 Unmodified Bituminous Binders

4.1.1 Physical Properties of Unmodified Bituminous Binders

This study performs penetration grade, softening point, and flash/fire point tests to determine the physical properties of bituminous binders. Table 3.2 shows that bituminous binders obtained from different refineries with the same penetration class exhibit different physical properties. Consequently, the bituminous binder obtained from the Batman refinery in the 50/70 penetration grade shows harder characteristics than the bituminous binder from the Kırıkkale refinery. Similarly, BM 70/100 is harder than KK70/100, as indicated by lower penetration and higher softening point.

4.1.2 Relationship Between SARA Fractions and Physical Properties

In this study, weight-based SARA fraction distributions of two different penetration grade bituminous binders obtained from Kırıkkale (utilizing imported crude oil sources - KK50/70 and KK70/100) and Batman (using domestic crude oil sources - BM50/70 and BM70/100) refineries were investigated. Based on the studies

conducted, it is observed that the SARA compositions of bituminous binders vary from refinery to refinery (Corbett, 1969; Michalica et al., 2008; Mirward et al., 2020; Plug et al., 2022). Figure 4.1 illustrates the distribution of SARA fractions of bituminous binders, which indicates significant differences between asphaltene and saturate fractions of bituminous binders. In contrast, a slight fluctuation is observed between the aromatic and resin fractions. It should also be highlighted that the repeatability of the weight-based SARA fraction analysis is significantly high based on the small variance in the trials. According to the Figure 4.1, it is concluded that the saturate fraction is influenced by the binder source and the distillation process of the crude oil in the refinery (Aljaafari & Ismael, 2020; Gawel & Czechowski, 1997; Mangiafico et al., 2016; Ren et al., 2022). In other words, the differences in the saturate fractions of the bituminous binders from the Batman and the Kırıkkale refineries arise due to the binder source.

As mentioned above, the asphaltene fraction in bituminous binders obtained from the Batman refinery is significantly higher than in the binders obtained from the Kırıkkale refinery. The asphaltene fraction within the bituminous binder affects its physical properties like penetration and softening point. As the asphaltene content increases, penetration decreases while the softening point rises (Aljaafari & Ismael, 2020; Mangiafico et al., 2016; Stangl, 2010; Zenke, 1977). When assessing the physical characteristics of bituminous binders in this study (See Table 3.1), the penetration values follow the order from smallest to largest, from BM50/70, KK50/70, BM70/100, to KK70/100. However, the pattern is not mirrored when analyzing the asphaltene fractions of the bituminous binders. The KK50/70 binder penetration is 48, with an asphaltene ratio of 18.4%, whereas the penetration of BM70/100 binder is 73, with an asphaltene ratio of 23%.

As the asphaltene fraction of the bituminous binder increases, penetration should decrease; however, this relationship is not observed between these two binders provided from different binder sources. This is because the maltene fractions based on the SARA analysis vary depending on the refinery or crude oil source. Similar findings were also reported by the work of Plug et al. (2022), in which bituminous

binders of (70/100 and 160/220) obtained from five different sources were investigated. The asphaltene fraction of the 160/220 penetration grade obtained from one source is higher than the percentage of the asphaltene fraction of the 70/100 penetration grade obtained from another source. Similarly, in this study, the asphaltene fraction percentage of the used BM70/100 binder is higher than that of the KK50/70 binder. In essence, the SARA composition of crude oil differs based on its origin and processing method, a difference that cannot be explained solely by physical properties. However, interpreting the physical properties on a refinery basis seems more feasible.

Considering the SARA fractions of the bituminous binder, it is established that asphaltene and resin fractions contribute to its hardening. In contrast, the aromatic and saturate fractions are recognized for their softening effects (Corbett, 1969). As mentioned, the asphaltene fraction directly affects the physical properties of the bituminous binder. As asphaltene content increases, the penetration value decreases while the softening point increases for a given source of binder. The saturate fraction is the lightest among the SARA fractions and responsible for its softening effect on the bituminous binder (Corbett, 1969; Porto et al., 2019). BM50/70 has a penetration value of 45 and a softening point of 54°C, while BM70/100 has a penetration value of 73 and a softening point of 51.5°C, indicating that BM50/70 is a harder bituminous binder. Thus, BM50/70 has more asphaltene fraction and simultaneously less saturate fraction. Similarly, KK50/70 has a penetration of 48 and a softening point of 52.5°C, while KK70/100 shows a penetration value of 77 and a softening point of 50°C. Upon analyzing their SARA compositions, KK50/70 contains higher amounts of asphaltene and lower saturates than KK70/100.

Furthermore, a comparison between bituminous binders obtained from the Batman and Kırıkkale refineries reveals that in terms of physical properties, BM50/70 is harder than KK50/70, with a higher asphaltene content and a lower saturate content. Similarly, BM70/100 binder exhibits greater physical hardness than KK70/100 binder, with a higher asphaltene content and a lower saturate content. Consequently,

binders obtained from the Batman refinery are harder compared to those obtained from the Kırıkkale refinery, revealed from physical properties and SARA fractions.

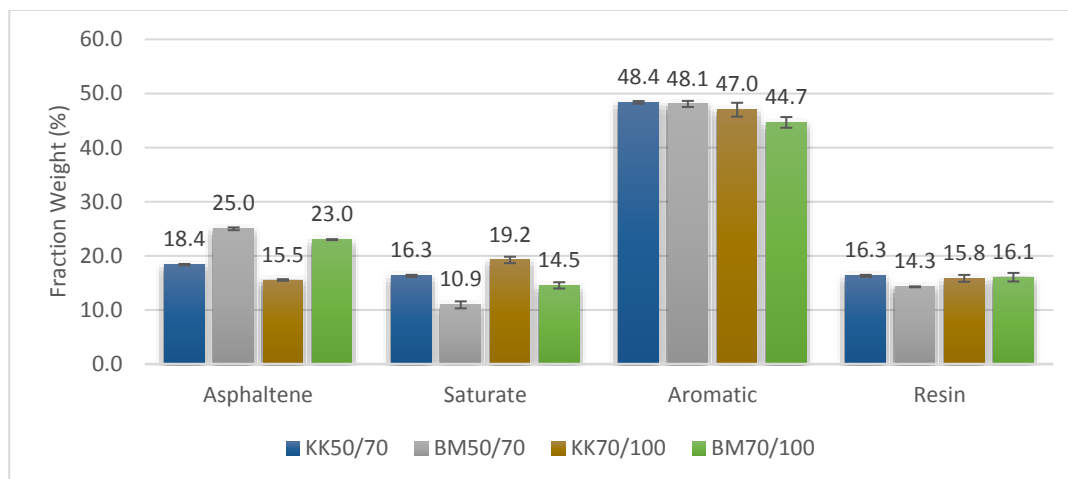


Figure 4.1. SARA fractions of unaged bituminous binders

Moreover, within the scope of the study, Brookfield Viscosity tests were conducted on the bituminous binders obtained from the Batman and Kırıkkale refineries. Measurements were taken at every 10°C between 120°C and 180°C and presented in Figure 4.2. Accordingly, BM50/70 has the highest viscosity, followed by KK50/70, while the viscosity of KK70/100 bituminous binder is the lowest. The studies in the literature demonstrate that SARA composition affects the viscosity of bituminous binders; it is known that among SARA fractions, the most significant impact on viscosity is the asphaltene fraction (Glover et al., 1987; Redelius & Soenen, 2015). As the asphaltene percentage in the bituminous binder increases, viscosity increases (Weigel & Stephan, 2018). It was measured that the asphaltene ratio was 25% for the BM50/70 binder and 23% for the BM70/100 binder. The higher asphaltene ratio in the BM50/70 binder correlates with increased viscosity. Similarly, the same trend was observed from the Kırıkkale binders. Additionally, the BM50/70 binder, having the highest asphaltene content, demonstrated the highest viscosity. Conversely, the KK70/100 binder, with the lowest asphaltene content, displayed the lowest viscosity among the bituminous binders tested.

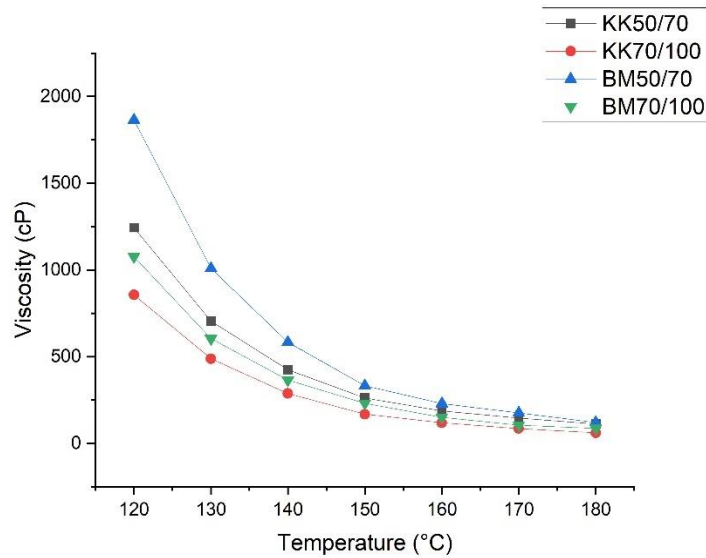


Figure 4.2. Viscosity results of unmodified bituminous binders

4.1.3 Rheological Properties of Unmodified Bituminous Binders

The bituminous binder has certain viscoelastic properties, displaying either viscous or elastic characteristics based on specific loads and temperatures (Liu et al., 2022; Li et al., 2015). The rheological properties of bituminous binders indicate the characteristics that change over a specific time concerning temperature and load frequency. To assess the viscoelastic properties under loading, hence the performance characteristic of the bituminous binder, two parameters are utilized: the complex shear modulus (G^*) and the phase angle (δ). Complex shear modulus (G^*) is the ratio of maximum shear stress to maximum shear strain, representing the resistance of the binder against deformation under shear stress. The other parameter is the phase angle (δ), representing the time lag between applied shear stress and the resultant shear strain. The phase angle indicates whether the bituminous binder demonstrates viscous or elastic behavior. If the phase angle is 90° , the bituminous binder shows entirely a viscous deformation behavior, whereas a phase angle of 0° signifies a purely elastic behavior.

The rutting and fatigue cracking are crucial distress types to be considered in asphalt pavement structures. Identifying the true grades of binders to indicate the rutting and fatigue resistance of bituminous binders is essential. The true grades are the maximum temperature that meets the rutting resistance criteria for unaged and short-term aged binders. The criterion for unaged bituminous binders is $G^*/\sin\delta \geq 1$ kPa, while for bituminous binders subjected to short-term aging, the criterion is $G^*/\sin\delta \geq 2.2$ kPa. Furthermore, for long-term aged bituminous binders, true grade represents the minimum temperature that fulfills the criterion is $G^*\sin\delta \leq 5000$ kPa. A higher true grade implies better rutting or fatigue resistance of the bituminous binder in hotter climates. A higher true grade can be achieved by a higher complex shear modulus (G^*) value and a lower phase angle (δ) value for the binder. It is known that an unaged bituminous binder has a lower complex shear modulus than a bituminous binder that has undergone short-term or long-term aging. It is shown that throughout the aging process, the complex shear modulus of binders exhibits a proportional increase (Liu et al., 2022).

The true grades of bituminous binders are also used to determine the Performance Grade (PG). The PG grade consists of two values; for instance, in PG64-12, '64' indicates the average maximum temperature of seven days, while '-12' signifies the minimum pavement temperature. The first value is determined from high and intermediate true temperatures in the DSR test, while the second is determined through the BBR test.

Table 4.1 shows the true grade of the bituminous binders used in this study and their corresponding high PG class. It can be observed that the true grades of the bituminous binders increase with aging. According to binder source, it becomes apparent that the unaged binders from the Batman refinery exhibit higher true grades than those from the Kırıkkale refinery, yet their PG classes are the same. Following the RTFO test, although the true grades of binders obtained from the Kırıkkale refinery increased, their PG classes remained unchanged. However, binders obtained from the Batman refinery experienced changes in both true grades and PG classes after oxidation, notably with PG grades increasing by two classes.

Table 4.1 Performance Grade (PG) of unmodified bituminous binders

Bituminous Binders	True Grades (°C)	Performance Grade (PG)
KK50/70	70.00	70
KK70/100	64.80	64
BM50/70	74.80	70
BM70/100	68.90	64
KK50/70 RTFO	74.40	70
KK70/100 RTFO	68.00	64
BM50/70 RTFO	82.80	82
BM70/100 RTFO	78.40	76
KK50/70 PAV	25.90	
KK70/100 PAV	21.00	
BM50/70 PAV	20.20	
BM70/100 PAV	19.70	

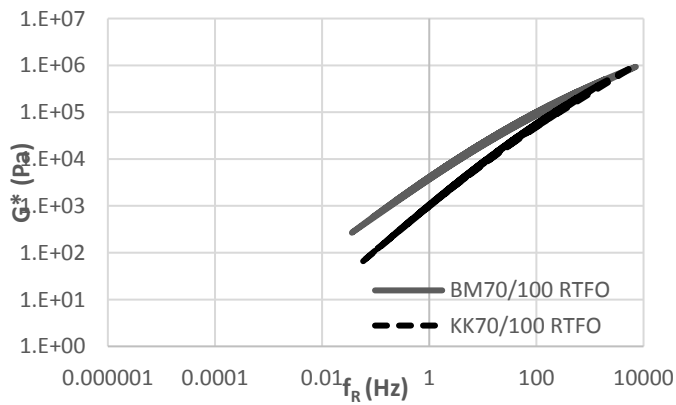
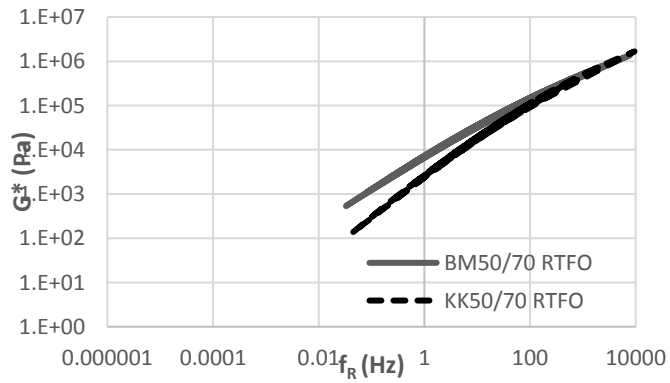
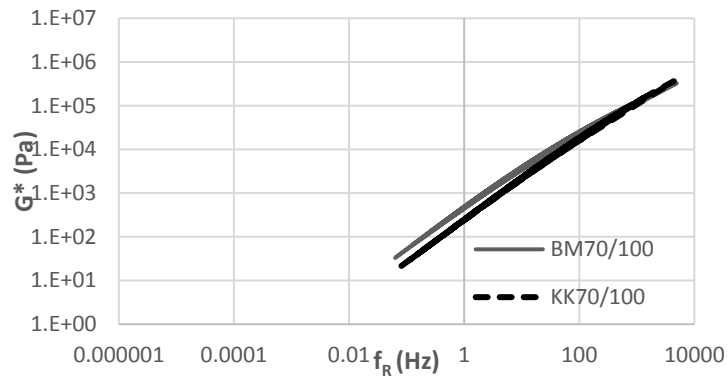
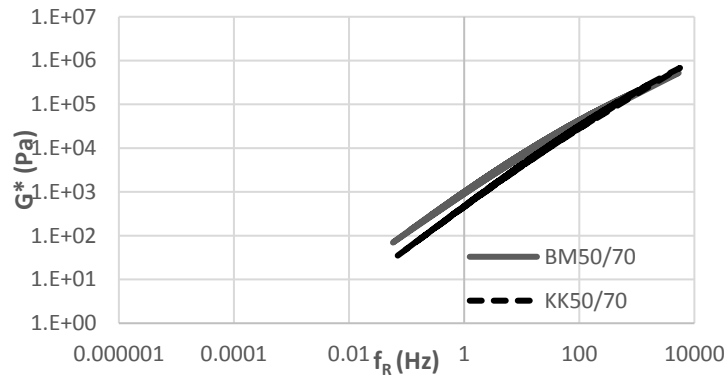
Frequency Sweep tests have also been conducted on bituminous binders. This test takes measurements 0.1 Hz to 10 Hz, starting from 34°C and increasing every 6°C up to 76°C. Table 4.2 shows variations in G^* and phase angle of bituminous binders observed at frequencies of 10 Hz within the range of 58°C and 76°C. BM50/70 exhibits the highest complex shear modulus at high temperatures, whereas KK70/100 shows the lowest. Moreover, KK70/100 demonstrates the highest phase angle, while BM50/70 displays the lowest. Therefore, the one with the highest rutting resistance among the binders is BM50/70, while the lowest is KK70/100. Regarding $G^*/\sin\delta$ values, the order is as follows: BM50/70, BM70/100, KK50/70, and KK70/100, and rutting resistance follows the same order. Consequently, binders from the Batman refinery show higher rutting resistance and exhibit a more elastic behavior than those from the Kırıkkale refinery.

Also, the rheological properties of the bituminous binder differ between high and intermediate temperatures. For instance, at intermediate temperatures, the rutting resistance of KK50/70 and KK70/100 binders is similar to that of BM50/70 and BM70/100. The rheological parameters of bituminous binders at intermediate temperature can be seen in Appendix.

Table 4.2 Unaged bituminous binders DSR results between 58-76°C at 10 Hz

f=10 Hz		Temperature (°C)			
Unaged Bituminous Binder		58	64	70	76
KK50/70	G*, Pa	22020.0	10740.0	5498.0	2992.0
	Phase Angle, δ	79.8	82.0	83.6	85.4
	G*/sin δ , kPa	22.4	10.8	5.5	3.0
KK70/100	G*, Pa	12340.0	6148.0	3222.0	1830.0
	Phase Angle, δ	81.9	83.9	85.4	85.9
	G*/sin δ , kPa	12.5	6.2	3.2	1.8
BM50/70	G*, Pa	31340.0	16150.0	8628.0	4781.0
	Phase Angle, δ	69.0	72.3	75.1	78.0
	G*/sin δ , kPa	33.6	17.0	8.9	4.9
BM70/100	G*, Pa	22990.0	12170.0	4912.0	2686.0
	Phase Angle, δ	71.2	74.1	78.9	80.7
	G*/sin δ , kPa	24.3	12.7	5.0	2.7

Furthermore, master curves are generated using the data obtained from the Frequency Sweep test results. Master curves provide a clearer illustration of the alterations in the rheological properties of bituminous binders. Figure 4.3 illustrates the frequency-dependent changes in the complex shear modulus within the temperature range of 34-76°C for the bituminous binders obtained from the refineries in Batman and Kırıkkale. The variation in the complex shear modulus of bituminous binders are evident with aging. Bituminous binders demonstrate an increase in stiffness and complex shear modulus as they undergo oxidation. Thus, while the binder source difference has less effect on the complex shear modulus of the bituminous binder when unaged, whereas, after long-term aging, the difference in the complex shear modulus values among bituminous binders (refer to BM50/70 PAV and KK50/70 PAV or BM70/100 PAV and KK70/100 PAV) becomes more distinct. As a result, the complex shear modulus of binders obtained from the Batman refinery are higher than those obtained from the Kırıkkale refinery in unaged, short-term, and long-term aging states.



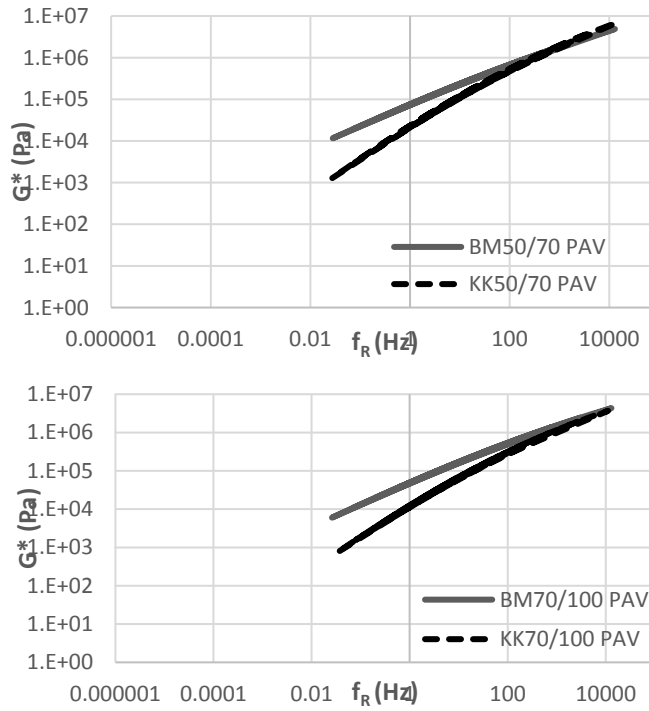
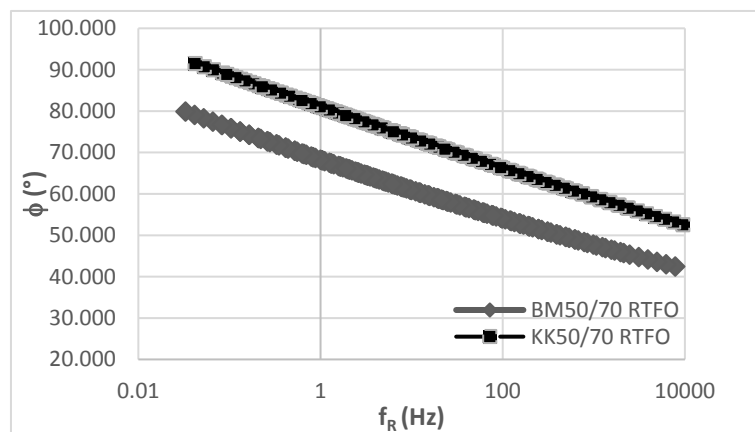
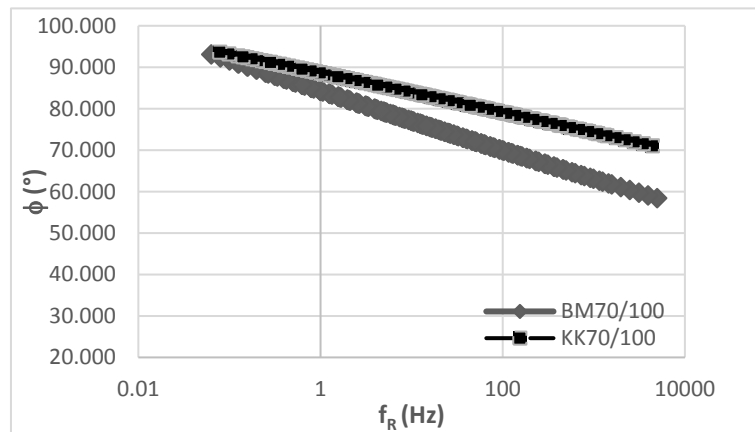
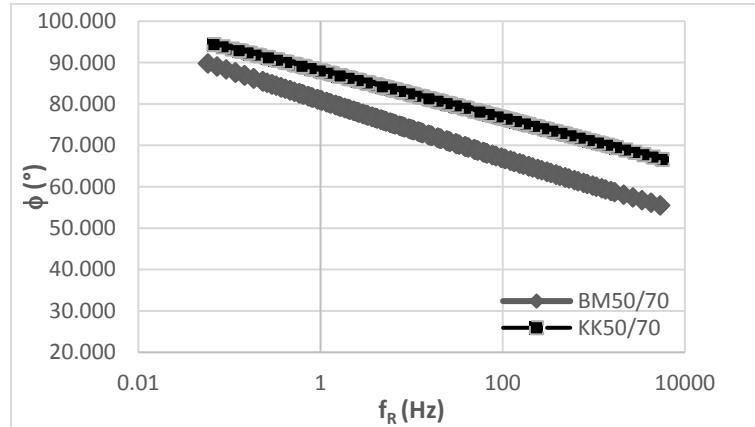


Figure 4.3. Master curves of bituminous binders exposed to aging (Complex shear modulus vs. Frequency)

Figure 4.4 shows the change in the phase angles of binders as the frequency increases within the temperature range of 34-76°C for the bituminous binders sourced from the refineries in Batman and Kırıkkale. The difference in phase angle values at low frequencies has significantly increased as bituminous binders are subjected to aging. At higher frequencies, the phase angles of binders obtained from the Kırıkkale refinery in unaged, short-term aged, and long-term aged conditions are greater than those obtained from the Batman refinery. Upon binder source, the difference in binder phase angle values increases with aging. This means that the phase angle values of binders change and decrease with aging. Particularly after short-term aging, it is more apparent that BM binders have a lower phase angle compared to KK binders. This trend becomes even more pronounced after long-term aging. As known, as the phase angle approaches 90°, the binder exhibits more viscous behavior, whereas nearing 0° indicates more elastic deformation behavior. Consequently, it is understood that binders obtained from the Batman refinery

exhibit more elastic deformation behavior compared to those from the Kırıkkale refinery.



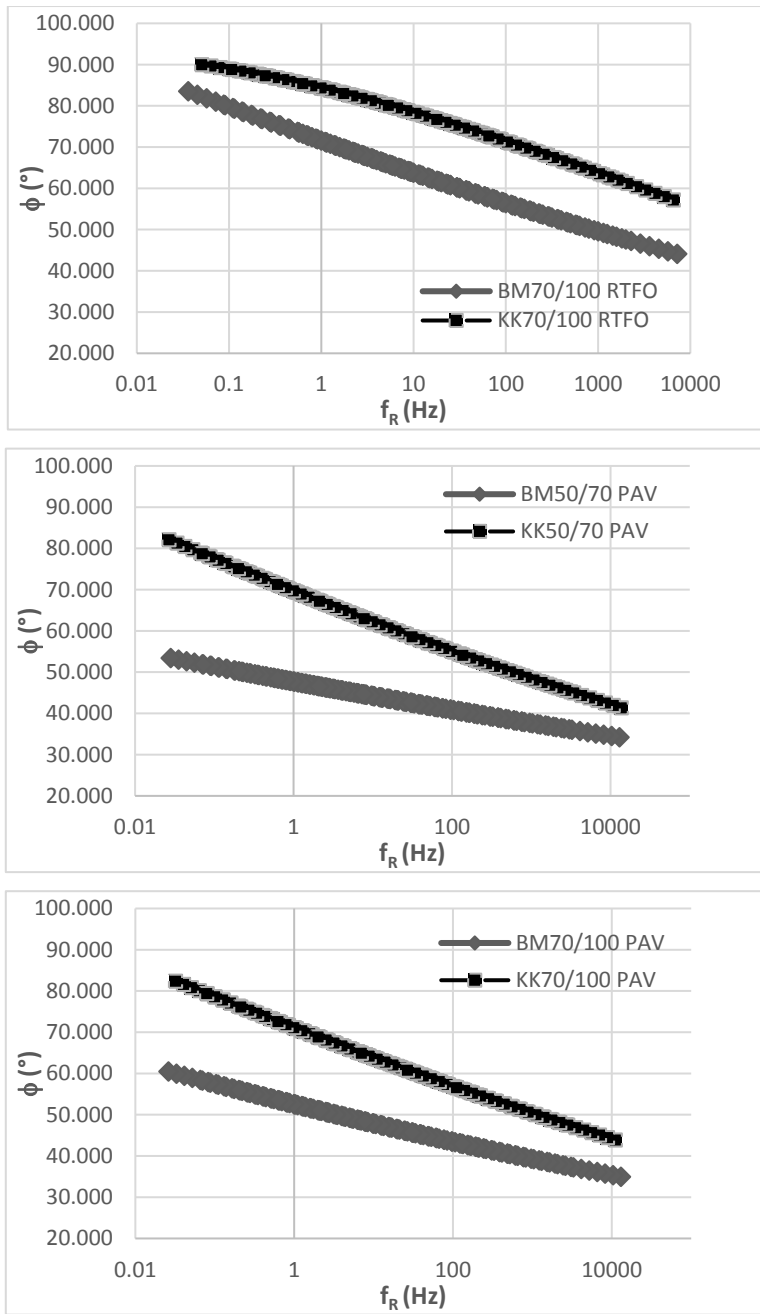


Figure 4.4. Master curves of bituminous binders exposed to aging (Phase angle vs. Frequency)

4.1.4 Relationship Between SARA Fractions and Rheological Properties

The rheological properties of bituminous binders are directly affected from the SARA compositions (Corbett & Merz, 1975; Glover et al., 1987; Redelius & Soenen, 2015). As emphasized in Chapter 2, when the bituminous binder undergoes aging, its aromatic fraction transforms into the resin fraction; then the resins transform into the asphaltene fraction. As a result of these transformations, the asphaltene fraction within the bituminous binder increases due to oxidation. On the other hand, it is known that the molecules of the saturate fraction resist oxidation. Thus, no significant change is expected in the saturate fraction throughout the aging. Consequently, significant changes occur, particularly in the asphaltene and aromatic fractions, while the saturate and resin fractions exhibit relatively minor changes with aging (Hashshenas et al., 2016; Mirwald et al., 2020).

The SARA compositions of unaged and aged bituminous binders of the 50/70 penetration grade obtained from the Batman and Kırıkkale refineries can be seen Figure 4.5 and Figure 4.6. It is known that exposure to aging leads to hardening of the bituminous binder due to the increase in the asphaltene fraction. It is observed that this increase is measured to be 3% and 4.8% in the BM50/70 and KK50/70 binders, respectively, after short-term aging. Accordingly, it can be concluded that the KK50/70 binder is more susceptible to short-term aging than the BM50/70. Moreover, it is observed that there is a decrease in the aromatic fraction of both binders at the end of short-term aging. Eventually, it is measured that the aromatic fractions are decreased by 4% and 7.3% in the KK50/70 and BM50/70 binders, respectively. Consequently, in the KK50/70 binder, a 4% decrease in aromatic content was observed, while asphaltene increased by 4.8%, indicating that a substantial portion of the aromatic fraction predominantly shifted towards the asphaltene fraction. However, within the BM50/70 binder, despite a 7.3% reduction in the aromatic fraction, the asphaltene fraction decreased by only 3%, signifying an imbalance. Thus, the changes in the saturate and resin fractions are also analyzed. While the saturate fraction slightly decreases by 0.3% in the KK50/70 binder, it

considerably increases by 1.6% in the BM50/70 binder. It can be concluded that KK50/70 is more susceptible to oxidation than BM50/70. Finally, it is observed that the resin fractions are decreased in both binders after short-term aging. This change is recorded as a decrease of 0.3% and 1.5% in KK50/70 and BM50/70, respectively.

After short-term aging, the bituminous binders were also subjected to long-term aging in PAV. The changes in SARA fractions of the KK50/70 and BM50/70 binders after long-term aging are also presented in Figure 4.5 and Figure 4.6. The asphaltene fraction of the KK50/70 binder increased by up to 4.6% after long-term aging, which also rose by 4.8% after short-term aging. However, after long-term aging, the aromatic fraction decreased by 8.4%, significantly higher than the decrease observed in the short-term aging stage. Eventually, the resin fraction increased by 1.1%. It can be concluded that some molecules transform from aromatic to resin fraction during aging. Additionally, the saturate fraction increased by about 0.7% after PAV, even though this change did not significantly alter the overall SARA composition. Similarly, for the BM50/70 binder, the asphaltene ratio increased by 3% after short-term aging and 8.7% after long-term aging (See Figure 4.6). It is observed that the asphaltene fraction of the BM50/70 binder significantly altered following PAV. However, its aromatic fraction decreased by 8.9% between short and long-term aging. In other words, the decrease in the aromatic fraction is compensated by the increase in the asphaltene fraction. On the other hand, both the saturate and resin fractions exhibited minor changes, which are not significant.

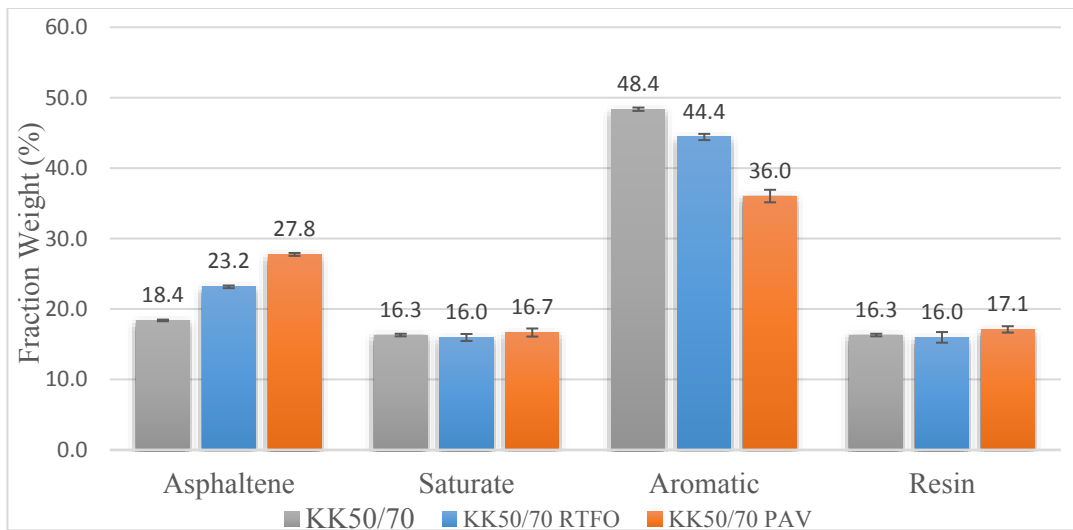


Figure 4.5. The change in SARA fractions of KK50/70 with short-term and long-term aging

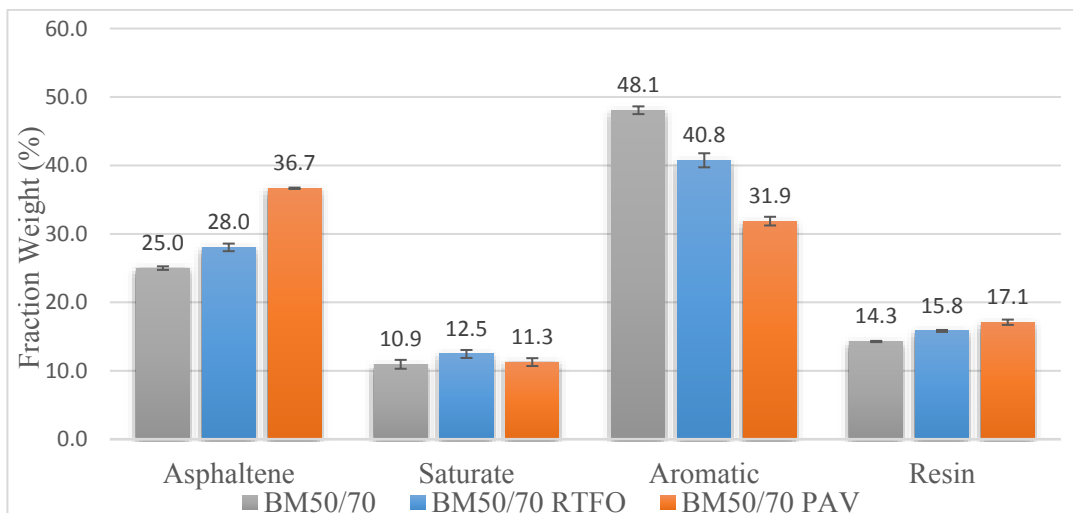


Figure 4.6. The change in SARA fractions of BM50/70 with short-term and long-term aging

Bituminous binders obtained from Batman and Kırıkkale refineries in the 70/100 penetration grades were examined separately (see Figure 4.7 and Figure 4.8). After short-term aging, it was observed that the asphaltene percentage of KK70/100

bituminous binder increased by 4.3%, whereas the asphaltene percentage of BM70/100 binder increased by 2.8%. Meanwhile, it is recorded that both binders (BM70/100 and KK70/100) show a 3.3% decrease in the aromatic fraction. In addition, the slight increase in resin fractions for both binders are recorded as 0.6% and 0.8% for BM70/100 and KK70/100 binders, respectively, which indicates the transformation of aromatics to resins. Additionally, when exposed to short-term aging, the saturate fraction of BM70/100 and KK70/100 binders exhibit $\pm 0.2\%$ change; hence, it can be inferred that both binders similarly resisted oxidation.

It has been observed that when studying the 50/70 penetration grade binders, the SARA fractions of bituminous binders are more significantly affected by long-term aging than short-term aging. Similarly, it is assessed that the asphaltene percentage of KK70/100 binder increased by 12.3% compared to the unaged binder after long-term aging, almost three times the impact of the short-term aging. Likewise, the asphaltene content of the BM70/100 binder increased by 3.8% and 12.1% after short and long-term aging, respectively. Therefore, it can be reported that the alteration in asphaltene content after long-term aging is approximately the same for BM70/100 and KK70/100 binders. For the aromatic fraction, KK70/100 binder experienced a decrease of 11%. Meanwhile, BM70/100 binder underwent a 14% reduction in its aromatic fraction. Additionally, the resin fraction increased by 1.3% and 2.1% in KK70/100 and BM70/100, respectively. As anticipated, this increase might stem from some aromatic molecules that fail to further convert into asphaltene and transform into resin rather than asphaltene.

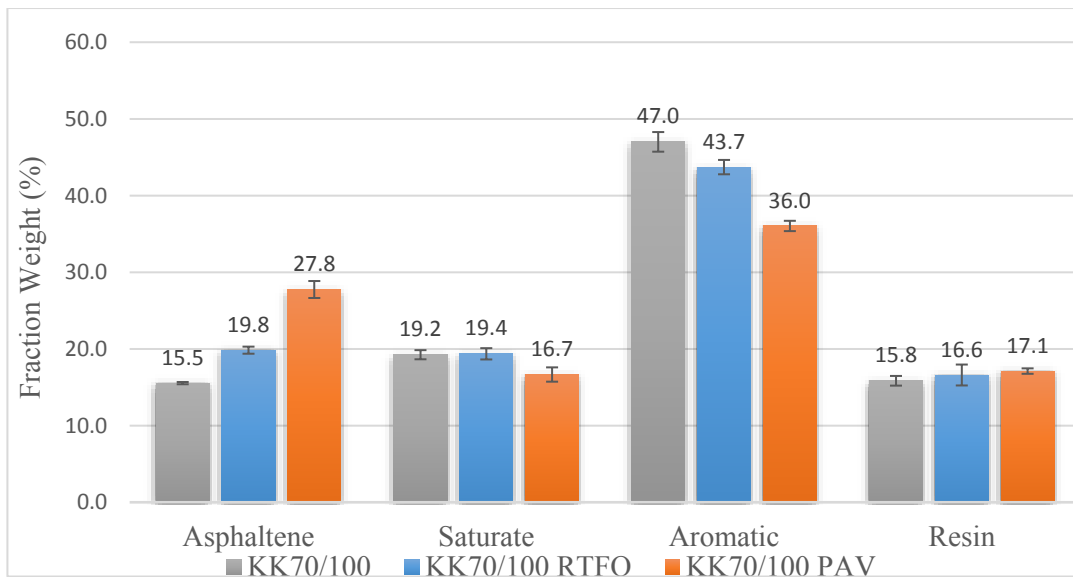


Figure 4.7. The change in SARA fractions of KK70/100 with short-term and long-term aging

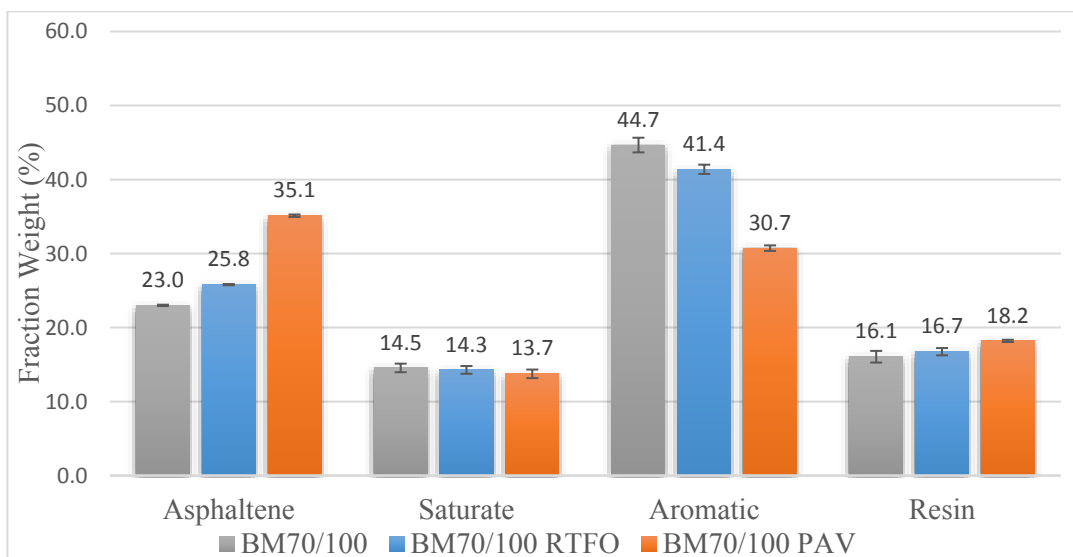


Figure 4.8. The change in SARA fractions of BM70/100 with short-term and long-term aging

According to the discussions above, specific conclusions have been drawn from SARA analyses of binders in both the 50/70 and 70/100 grades obtained from both Batman and Kırıkkale refineries. The asphaltene fraction showed an increase in the range of 2.8% to 4.8% after RTFO, whereas after PAV, it exhibited an increase of 9.4% to 12.3%. Long-term aging notably affected the asphaltene fraction of binders explicitly obtained from the Batman refinery more than those from the Kırıkkale refinery. The aromatic fraction decreased by approximately 3.3% to 7.3% with short-term aging, followed by a decrease of 11% to 16.2% after long-term aging. Regarding the saturate fraction, an alteration in the range of 0.2% to 2.5% was observed after both short and long aging periods. However, it is not expected to impact the SARA composition significantly. While the resin fraction showed a slight change in the range of 0.3% to 1.5% after short-term aging, the change during long-term aging ranged between 0.6% and 1.5%, reflecting a slight alteration. On the other hand, it is observed that the resin fraction marginally increased in some samples and decreased in others at the end of short-term aging. However, during long-term aging, it consistently showed a slight increase. It could be considered that the long-term aging process significantly impacted the resin fraction. Ultimately, when subjected to aging, the SARA fractions of bituminous binders undergo the following changes: asphaltene increases, saturate changes very minimally or remains unchanged, aromatic fraction decreases, and the resin fraction undergoes slight changes or remains constant after short-term aging but exhibits a very slight increase after long-term aging.

From this point on, it is aimed to evaluate and discuss the alterations within SARA fractions and their influence on the rheological characteristics of bituminous binders. It is known that the amount of the asphaltene fraction in the bituminous binder directly impacts the rheological properties of the bituminous binder (Sultana & Bhasin, 2014; Zheng et al., 2020). It is expected that when the asphaltene content is high in the bituminous binder, its rutting resistance is better. Thus, it possesses a higher complex shear modulus and lower phase angle. This interpretation implies that the bituminous binder exhibits more elastic behavior (Michalica et al., 2008;

Lu & Isocsson, 2002; Weigel & Stephan, 2018). In addition, there is a relationship between the complex shear modulus and SARA fractions. As the asphaltene and resin fractions within the bituminous binder increase, the complex shear modulus also increases. However, it should be recalled that an increase in the aromatic fraction leads to a decrease in complex shear modulus (Xiao & Wang, 2022; Wang et al., 2019).

This section presents the relationship between the asphaltene and maltene fractions of bituminous binders exposed to short-term and long-term aging and their complex shear modulus (G^*) and phase angle (δ), presented in Appendix. For ease of discussion, the complex shear modulus and phase angle values were tabulated at a frequency of 10 Hz for both 34°C and 76°C. It is known that bituminous binders harden and lose elasticity as they undergo aging. Based on the results, it is evident that the asphaltene fraction of the bituminous binder increases with aging and that the maltene fraction decreases with aging. Moreover, an increase in the asphaltene fraction within the binder corresponds to an increase in the shear modulus and a decrease in the phase angle. In other words, as the bituminous binder ages, the asphaltene fraction increases, leading to hardening and increased stiffness, subsequently elevating the shear modulus and reducing the phase angle. On the other hand, a direct correlation between the aromatic fraction of bituminous binders and complex shear modulus has not been established; therefore, considering the total maltene fraction might be more suitable for this study.

According to this study, the BM50/70 binder has the highest asphaltene content in unaged, short-term, and long-term aging conditions while possessing the highest complex shear modulus and the lowest phase angle. Conversely, the KK70/100 binder has the lowest asphaltene content, the lowest complex shear modulus, and the highest phase angle. Therefore, regarding the rutting resistance of bituminous binders, the one with the highest asphaltene content, BM50/70, demonstrates the highest resistance, followed by BM70/100, KK50/70, and KK70/100. Regarding phase angle, the highest value, KK70/100, exhibits more viscous behavior than the other binders, whereas BM50/70, with the lowest phase angle, demonstrates more

elastic deformation behavior. It can be concluded that as the phase angle increases, the asphaltene content decreases while the maltene fraction increases.

4.1.5 Gaestel Index of Unmodified Bituminous Binders

The Gaestel Index (I_c) of the bituminous binders in their unaged state is presented in Figure 4.9. Upon examining the I_c values of binders obtained from different refineries. It is known that I_c values increase with asphaltene (Nunes et al., 2022). Due to the small differences in the asphaltene contents of the bituminous binders used, this correlation is not established. Additionally, upon observing Figure 4.9, it is apparent that all binders exhibit gel-type behavior and are unstable. If the I_c value of the binder exceeds 0.5, it is known that the binder hardens. Reasons for the inability to establish a correlation between the I_c value and asphaltene content of the binders may be due to the irregular distribution of asphaltene micelles, their unstable behavior, and as well, the similarity in asphaltene ratios, leading to closeness in the I_c values as well. Sakib (2018) reported no correlation between I_c and rheological properties.

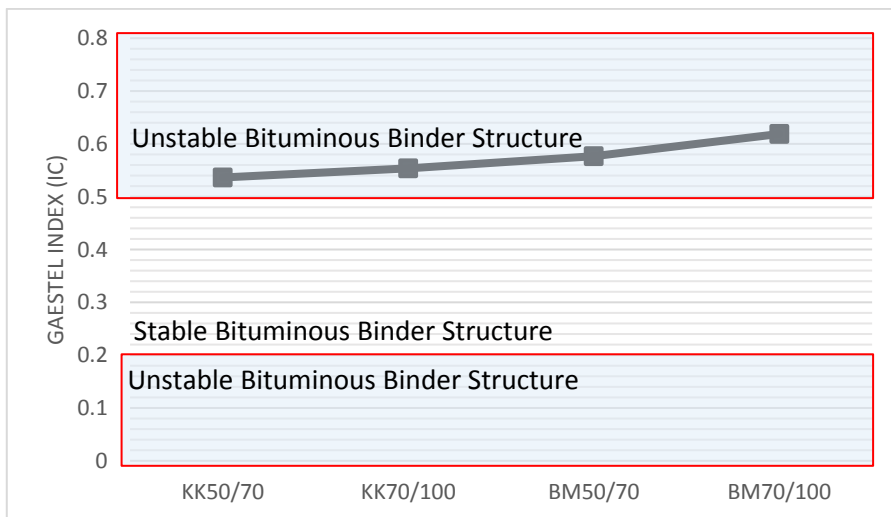
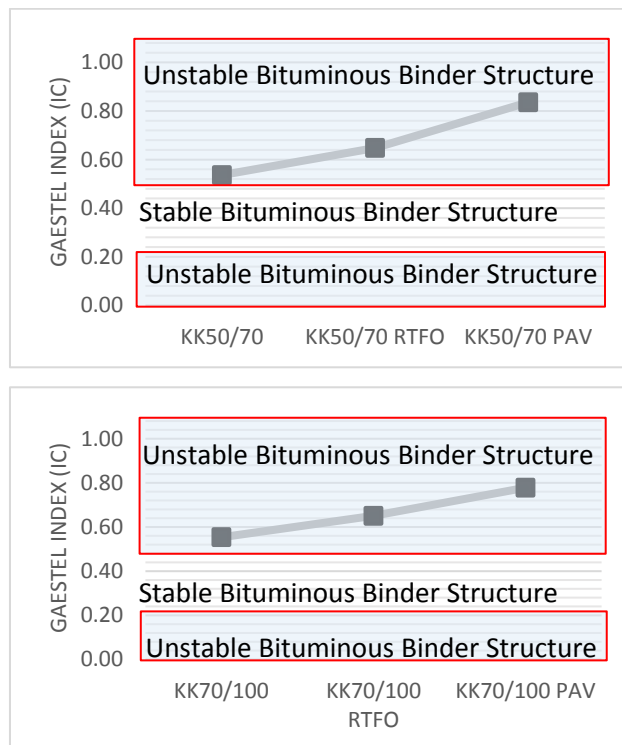


Figure 4.9. Gaestel Index of unmodified bituminous binders

Although a correlation with the Gaestel Index cannot be established in the unaged state of bituminous binders, the Gaestel Index of these binders increases with aging. The asphaltene content of these binders also increases with aging, and it is observed that as asphaltene content rises, the Ic value increases accordingly in Figure 4.10.

Binders obtained from the Batman refinery exhibit a much greater increase in Ic values after long-term aging than those obtained from the Kırkkale refinery. The Ic values of BM50/70 and BM70/100 binders reach to 1.0, while the KK50/70 and KK70/100 binders have Ic values of 0.84 and 0.78 after long-term aging, respectively. Consequently, it is evident that binders obtained from the Batman refinery demonstrate more instability and exhibit a stronger tendency toward gel-type behavior after aging compared to those obtained from the Kırkkale refinery. Moreover, the Ic value, the penetration value, asphaltene content, and complex shear modulus values also prove that binders from the Batman refinery are harder than those obtained from Kırkkale.



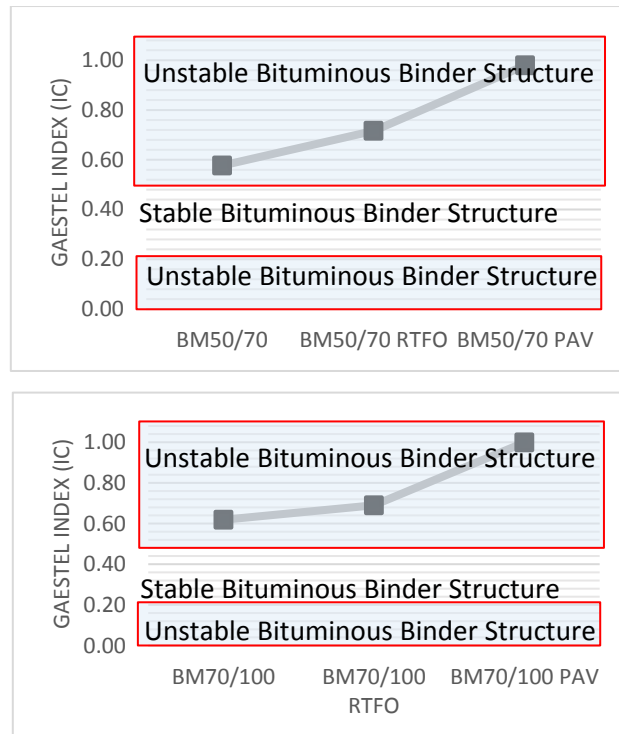


Figure 4.10. Change of Gaestel Index with aging

4.1.6 FTIR Analysis Results of Unmodified Bituminous Binders

The functional groups of bituminous binder are related to the physical and rheological properties of the bituminous binder (Ren et al., 2023). FTIR analysis was conducted on unmodified bituminous binders to examine their functional groups. Figure 4.11 shows the FTIR spectra of unmodified bituminous binders within the wavenumber range of 4000-400 cm^{-1} . Upon examining the peak heights in the spectra of bituminous binders, two peaks are visible within the 3000-2800 cm^{-1} range. These peaks indicate the presence of C-H stretching in the functional groups of the bituminous binder. Furthermore, N-H bending in the range of 1580-1650 cm^{-1} , C-H bending around 1450 cm^{-1} , O-H bending within 1330-1420 cm^{-1} , C-O stretching between 1020-1075 cm^{-1} , and C-H bending in the range of 700-900 cm^{-1} are observed for unmodified bituminous binder from Kırıkkale and Batman

refineries. Figure 4.11 shows that the binder with the highest intensity is BM50/70, followed by KK50/70. BM70/100 and KK70/100 have nearly the same intensity.

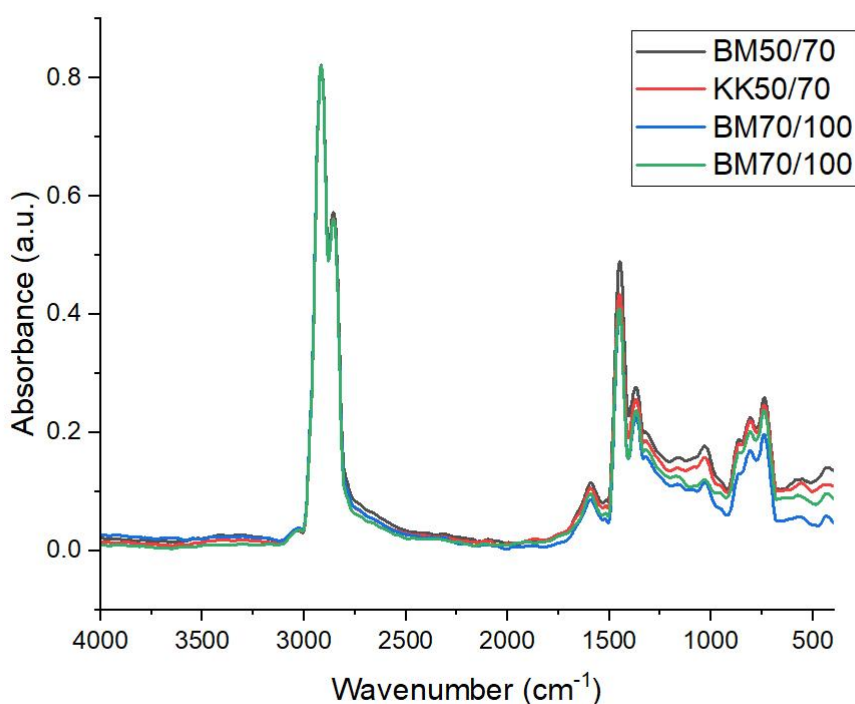


Figure 4.11. FTIR Spectra of unmodified bituminous binder

The carbonyl index and sulfoxide index are initially examined to determine the Aging Index values of bituminous binders. As the bituminous binder ages, the aliphatic sulfide group transforms into a sulfoxide group, while the benzylic carbon group converts into carbonyl (Liu et al., 2014). In other words, the carbonyl and sulfoxide indexes of bituminous binders are affected by exposure to oxidation.

Figure 4.12 depicts the changes in the carbonyl and sulfoxide indexes of bituminous binders obtained from the Kırıkkale refinery due to aging exposure. It is observed that the carbonyl and sulfoxide indexes of both penetration-grade binders increase with exposure to aging. While the carbonyl index of the KK50/70 binder is

minimally affected by short-term aging, the carbonyl index of the KK70/100 binder is notably impacted by short-term aging. Following long-term aging, the carbonyl indexes of KK50/70 and KK70/100 binders are very close. Additionally, it is evident that the sulfoxide indexes significantly increase with both short-term and long-term aging for both binders.

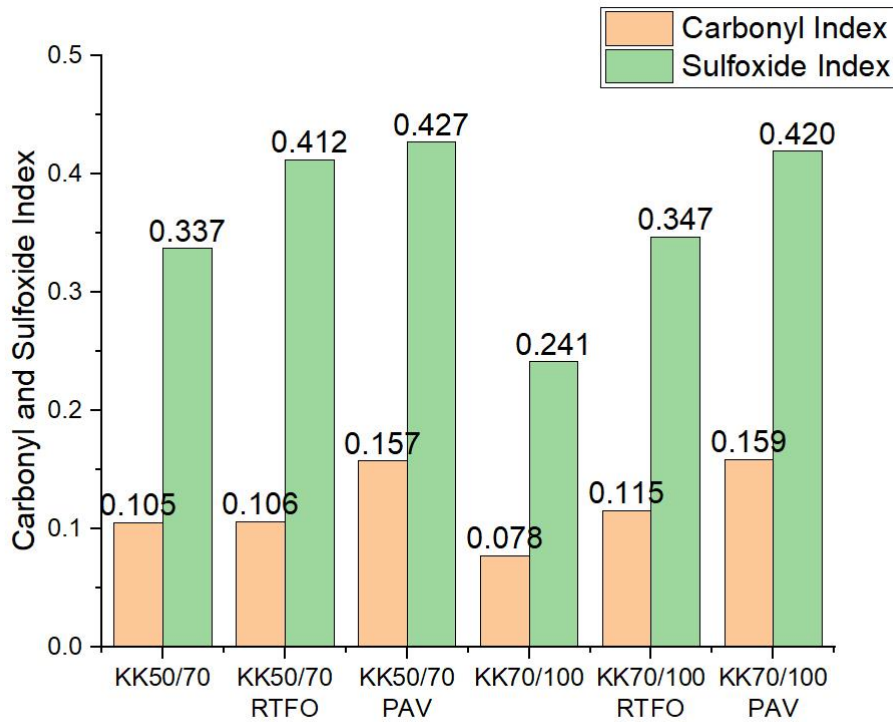


Figure 4.12. Change of the carbonyl and sulfoxide indices of bituminous binder due to aging (Kırıkkale refinery)

Figure 4.13 illustrates the alterations in carbonyl and sulfoxide indices of binders, namely BM50/70 and BM70/100, sourced from the Batman refinery after short-term and long-term aging procedures. It is evident that the carbonyl and sulfoxide indexes of the BM50/70 binder increase with aging over time. Conversely, after short-term aging, a slight decline is observed in the carbonyl index of the BM70/100 binder. Carbonyl and sulfoxide groups of bituminous binders can be more influenced by

long-term aging processes rather than short-term aging (Koyun et al., 2022). For instance, the change in the carbonyl index of bituminous binders during short-term aging is related to certain functional groups that form during the short-term aging process. The reason for the lack of impact on the carbonyl index of the bituminous binder due to short-term aging is the limited production of certain oxygen-containing polar functional groups in significant quantities (Jiang et al., 2021). However, upon subjecting BM70/100 to long-term aging, a noticeable escalation in both carbonyl and sulfoxide indices becomes more pronounced.

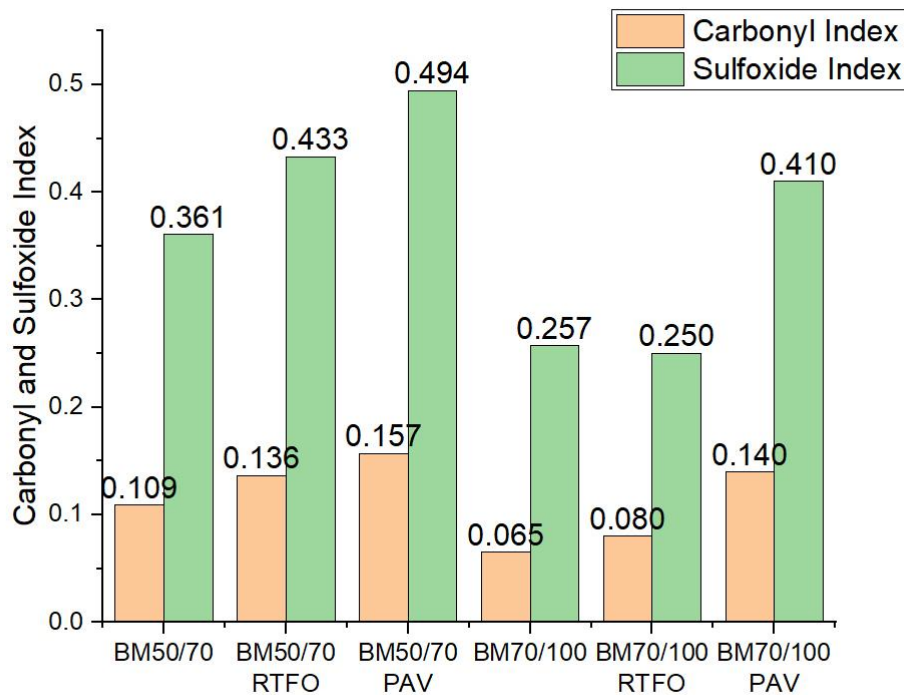


Figure 4.13. Change of the carbonyl and sulfoxide indices of bituminous binder due to aging (Batman refinery)

The determination of the thermal oxidation of bituminous binder is based on the elevation observed in the carbonyl and sulfoxide indices (Mirwald et al., 2022). In this study, the sulfoxide and carbonyl index of the BM50/70 binder is higher than

that of the KK50/70 binder. Additionally, the sulfoxide and carbonyl index of BM50/70 is higher than KK50/70 after short-term aging. Therefore, following a short-term aging process, the thermal oxidation of the BM50/70 binder exceeds that of the KK50/70. Following the long-term aging process, the sulfoxide indices of BM50/70 and KK50/70 binders are the same. Furthermore, the carbonyl and sulfoxide indices of KK70/100 binder are higher than those of BM70/100 and the binder exhibiting greater thermal oxidation is KK70/100.

Aging Index (AI_{FTIR}) is determined by summing the areas of the carbonyl group ($1660-1800\text{ cm}^{-1}$) and the sulfoxide group ($984-1079\text{ cm}^{-1}$), and then dividing this total by the area of an aliphatic group ($1350-1525\text{ cm}^{-1}$) which serves as the reference area. Figure 4.14 displays the aging index values of unmodified bituminous binders. The aging index value rises with the hardening of the bituminous binder and decreases with its softening. The penetration value of the BM50/70 binder is lower than that of the BM70/100 binder, indicating it is harder. Similarly, the KK50/70 binder is harder compared to the KK70/100. Furthermore, The BM50/70 binder holds the highest aging index, followed by the KK50/70 binder, sequentially by BM70/100 and KK70/100 binders. There's a clear relationship between the binders' aging index values and their physical hardness. BM50/70, the hardest binder, aligns with the highest aging index value. Regarding physical properties, KK70/100, the softest binder, also displays the lowest aging index.

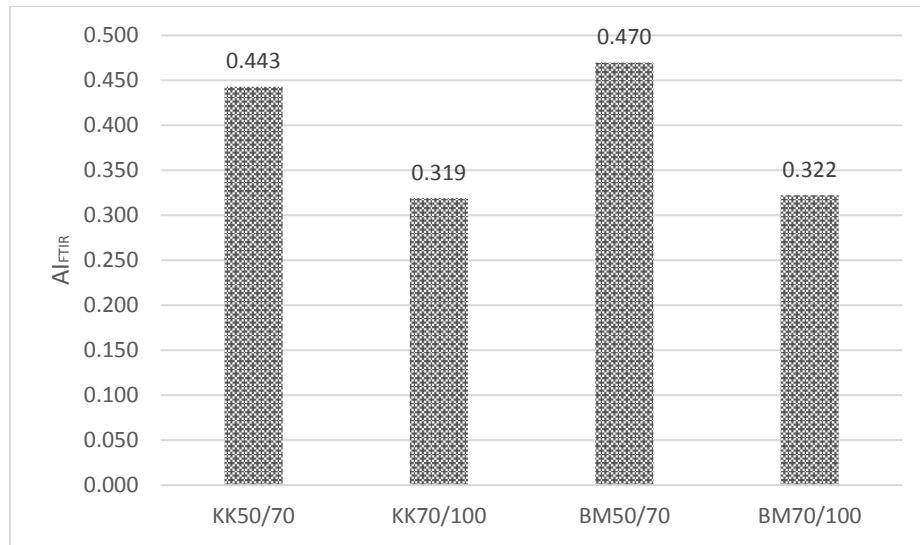


Figure 4.14. Aging Indices of unmodified bituminous binders

Figure 4.15 illustrates the change in aging index values of binders sourced from Kırıkkale Refinery through aging. The binders obtained from the Kırıkkale Refinery show an increase in the aging index following both short-term and long-term aging. Similarly, Figure 4.16 illustrates the variations in the Aging Index due to exposure to aging for the bituminous binders obtained from the Batman Refinery. The Aging Index of BM50/70 binder consistently increases after both short-term and long-term aging. On the other hand, it's observed that BM70/100 binder is minimally affected by short-term aging but significantly impacted by long-term aging, showing a more pronounced effect.

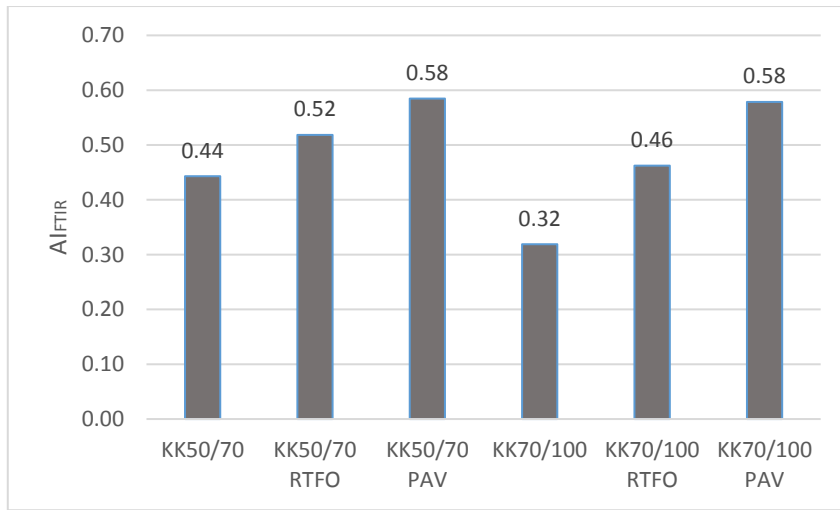


Figure 4.15. Aging Indices of bituminous binder obtained from Kırıkkale refinery

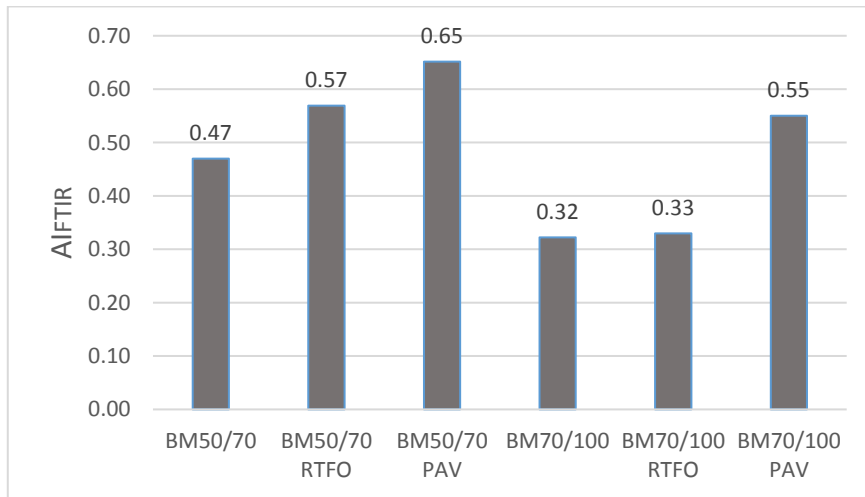


Figure 4.16. Aging Indices of bituminous binder obtained from Batman refinery

Furthermore, a relationship exists between the Gaestel index and aging index values of unmodified bituminous binders (Kleizienė et al., 2019). Unmodified bituminous binders exhibit an increase in Gaestel indices when subjected to aging, accompanied by a rise in aging indices obtained from FTIR. Table 4.3 illustrates the increase in Gaestel indices and aging indices of binders following short-term and long-term aging. Furthermore, the relationship between the Gaestel indexes and aging indexes

of bituminous binders is also presented in Figure 4.17. A linear correlation has been identified between the Gaestel indexes and aging indexes of bituminous binders, and it has been formulated for each binder.

Table 4.3 Relationship between Gaestel Index and AI_{FTIR}

	Gaestel Index (Ic)	AI_{FTIR}
KK50/70	0.536	0.443
KK50/70 RTFO	0.648	0.519
KK50/70 PAV	0.836	0.585
KK70/100	0.554	0.319
KK70/100 RTFO	0.650	0.462
KK70/100 PAV	0.778	0.579
BM50/70	0.577	0.470
BM50/70 RTFO	0.716	0.569
BM50/70 PAV	0.979	0.651
BM70/100	0.619	0.322
BM70/100 RTFO	0.690	0.330
BM70/100 PAV	0.999	0.550

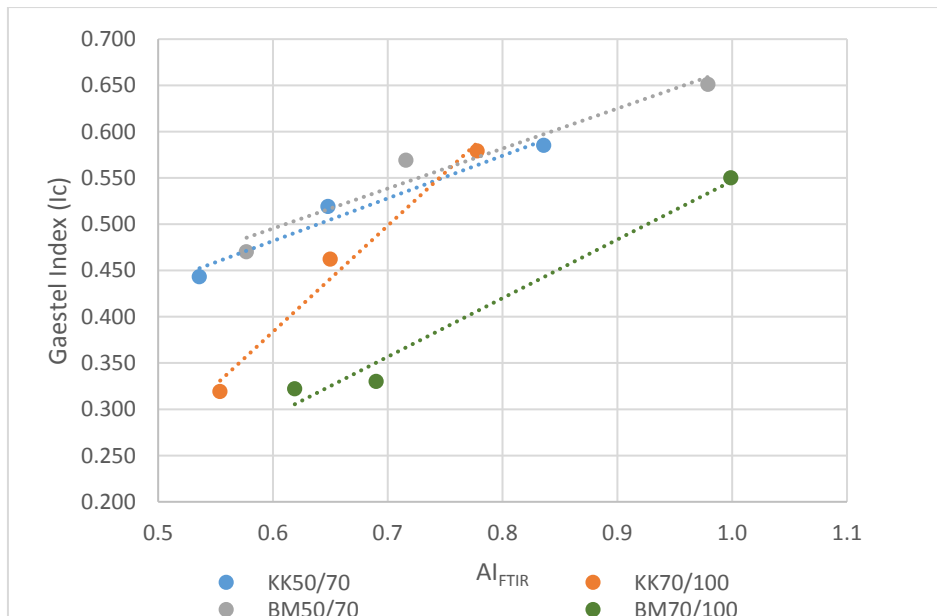


Figure 4.17. Gaestel Index and Aging Index of unmodified bituminous binders

4.2 Modified Bituminous Binders

4.2.1 Physical Properties of Modified Bituminous Binders

Modification with WMA additives changes the physical properties of bituminous binders. In this study, the 50/70 penetration grade binders obtained from the Kırıkkale and Batman refineries are modified with 1.5% Sasobit and 0.5% Evotherm, as discussed in Chapter 3 Materials and Method. It is aimed to understand how binders with the same penetration grades but different chemical structures are affected by the WMA modification. It should be reminded that the physical properties have already been presented in Table 3.3 and Table 3.4 in Chapter 3. It is known that the addition of Sasobit results in the hardening of the bituminous binder, in other words, reduces the penetration. It is observed that the penetration values of KK50/70 and BM50/70 binders reduces from 48 to 44 and from 45 to 42, respectively. Moreover, the softening points of KK50/70 and BM50/70 binders increased by 3°C and 5.5°C, respectively. On the other hand, the Evotherm additive increases the penetration value of the KK50/70 binder from 48 to 52 and the penetration value of the BM50/70 binder from 45 to 53. The addition of the Evotherm additive reduced the softening point value of KK50/70 binder by 2°C and the softening point value of BM50/70 binder by 2.5°C. Consequently, it can be concluded Sasobit reduces the penetration value of the bituminous binder and increases the softening point, while Evotherm increases the penetration value and decreases the softening point. In other words, Sasobit hardens the bituminous binder, while Evotherm softens it. Furthermore, the flash and fire points have decreased in both modified bituminous binders. However, it is observed that there is a more significant decrease when modified with Evotherm compared to Sasobit.

It should be highlighted that the viscosities of the bituminous binders modified with Sasobit and Evotherm have also changed (Figure 4.18 and Figure 4.19). It has been observed that the addition of Sasobit and Evotherm leads to a decrease in the high-

temperature viscosity of bituminous binders obtained from both refineries. The viscosity results were more influenced by the addition of Sasobit than by Evotherm. In other words, the consistency of the bituminous binder has been more affected by adding Sasobit than by adding Evotherm to the bituminous binder.

According to the 2010 EAPA publication "The use of WMA," chemical additives do not affect the viscosity of bituminous binders. While Sasobit is an organic additive, Evotherm is a chemical additive that does not affect viscosity. On the other hand, organic and foaming process additives reduce the viscosity of bituminous binders. A study also proves that Evotherm does not affect the viscosity of bituminous binders. The study modified the bituminous binder with a 0.4% ratio of Evotherm additive and observed that Evotherm had no significant effect on viscosity. Nevertheless, when the bituminous binder is modified with Sasobit, its viscosity decreases (Yero & Hainin, 2012; Zhang et al., 2015).

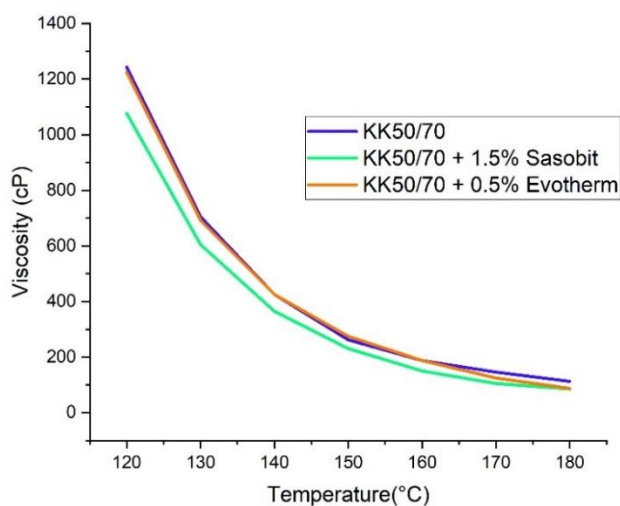


Figure 4.18. The effect of WMA additives on the viscosity of bituminous binders (Kırıkkale Refinery)

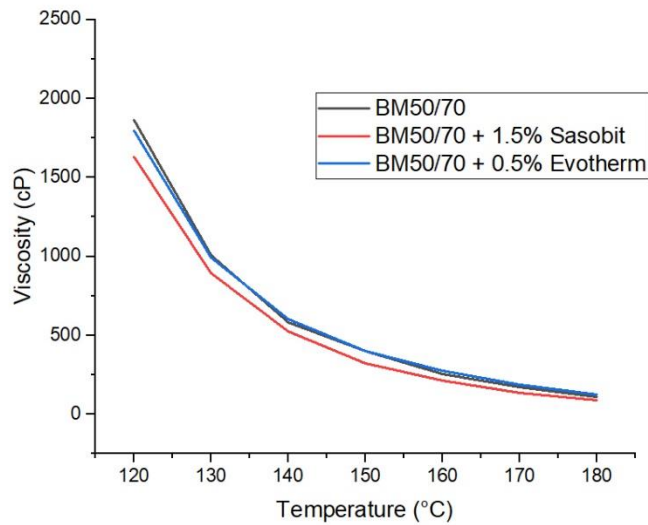


Figure 4.19. The effect of WMA additives on the viscosity of bituminous binders (Batman Refinery)

4.2.2 Relationship Between SARA Fractions and Physical Properties

WMA additives affect not only the physical properties but also the chemical properties of the bituminous binder. The knowledge about the impact of WMA additives on SARA fractions, these fractions have not been elucidated yet (Autelitano et al., 2017; Cao et al., 2009; Oyan & Sakib, 2022; Zhang et al., 2023). Only, Adepu et al. (2023) studied the effect of Sasobit additive on asphaltene and maltene fractions, and it was reported that Sasobit increases the asphaltene content and decreases the maltene content. Thus, this study is valuable as it comprehensively considers the SARA fractions and physical properties.

Figure 4.20 shows the changes in SARA fractions of bituminous binders obtained from the Kırıkkale refinery (KK50/70) after the WMA additive additions. It is known that as the penetration value decreases, the asphaltene fraction increases. Therefore, the Sasobit results in an increase in the asphaltene content by approximately 0.7%.

Additionally, Sasobit has a very slight effect on the saturate and aromatic fractions. While the saturate fraction increased by 1.6%, the aromatic fraction decreased by as much as 0.9%. Also, the resin content has decreased by approximately 3%. It is known that saturate and aromatic fractions from SARA fractions soften the bituminous binder, while asphaltene and resin fractions harden it (Corbett, 1969). After the addition of Sasobit, the decrease in penetration and the increase in softening point of the bituminous binder (See Table 3.3). As Sasobit hardens the KK50/70 binder, the increase in asphaltene and the decrease in aromatic fractions are consistent. However, the increase in the saturate fraction and decrease in the resin fraction do not align with the physical properties of the bituminous binder. Similarly, Figure 4.21 represents the changes in BM50/70 binders with WMA additives. When the Sasobit additive was added to the BM50/70 binder, the binder's asphaltene and saturate contents increased by 1.1%, and 2.2%, respectively. Meanwhile, the aromatic and resin contents decreased by 2.3% and 1.2%, respectively. The change in the SARA fractions of bituminous binders obtained from different refineries occurred similarly with the addition of Sasobit. However, while the aromatic fraction decreases by 0.9% in KK50/70, it decreases by 2.3% in BM50/70, or the resin fraction decreases by 3% in KK50/70 as it decreases by 1.2% in BM50/70. These slight differences may stem from the binder source and processing. Consequently, it can be reported that it increases the asphaltene and saturate fractions while reducing the aromatic and resin fractions. Thus, the fractions linked to the physical properties of the bituminous binder may be asphaltene and aromatic fractions, rather than the saturate and resin fractions, as they are more suitable for correlating with their physical characteristics.

In Figure 4.20, the change in SARA contents is observed when the Evotherm additive is added at a rate of 0.5% to the KK50/70 binder. The Evotherm additive has reduced the asphaltene fraction content by 0.7% while decreasing the resin and saturate contents by 2.6%. The aromatic content, on the other hand, has increased by 4.4%. As seen in Table 3.3, the Evotherm additive softens, resulting in an increase the penetration value and reduction in the softening point temperature. Upon

modification of the KK50/70 binder with Evotherm additive, there has been a reduction in asphaltene and resin contents, an elevation in the aromatic fraction, and consistent alterations in its physical properties. On the other hand, the saturate fraction also decreased. Similarly, Evotherm additive was added to the BM50/70 binder (see Figure 4.21), and the asphaltene and resin contents decreased by 0.6% and 2.7%, respectively. The aromatic and saturate contents have increased by 0.8% and 0.7%, respectively. Upon examining the physical properties of BM50/70 (Table 3.4), it is evident that the Evotherm additive softens the BM50/70 binder, like the KK50/70 binder. The SARA fractions of the BM50/70 and KK50/70 binders have changed in a way that demonstrates the softening effect of the binder. However, the increase in aromatic ratio is much more apparent in the KK50/70 binder compared to the BM50/70 binder.

As a result, when the Evotherm additive is added to the binder at a rate of 0.5%, it reduces the asphaltene and resin fractions while increasing the aromatic fraction. The saturate fraction exhibited different trends in BM50/70 and KK50/70 bituminous binders, decreasing by 2.6% in KK50/70 while increasing by 0.7% in BM50/70. Even before the modification of bituminous binders, the saturate fractions of the binders were noticeably different, stemming from variations in binder sources. The alteration in the saturate fraction due to the Evotherm additive can also be interpreted as a change dependent on the binder source, reflecting the response of the bituminous binder's saturate fraction to the Evotherm additive.

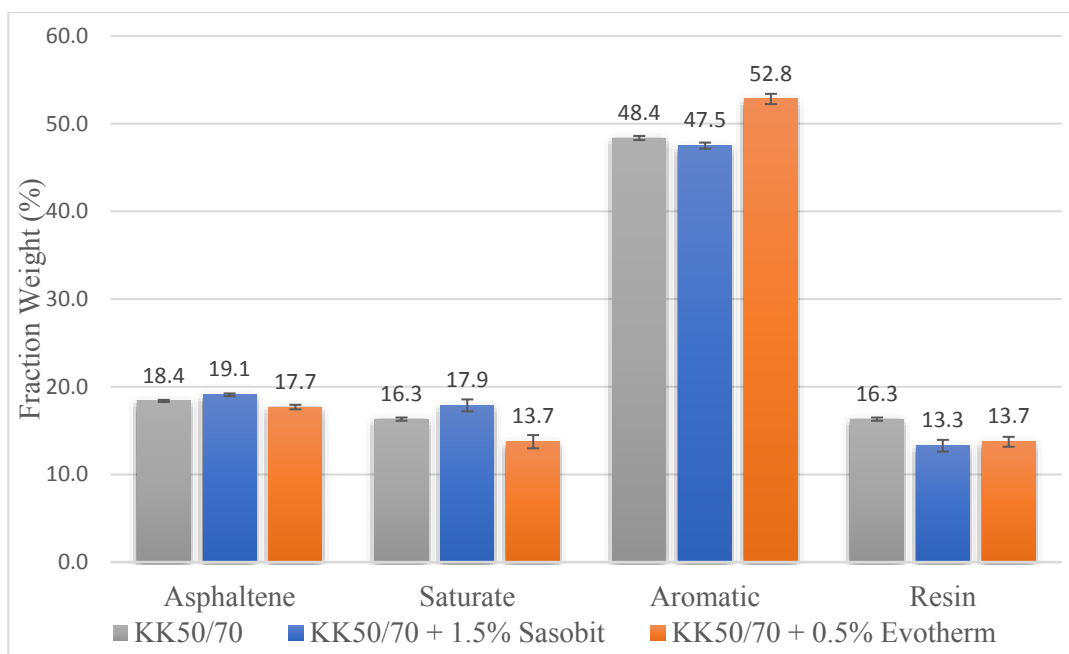


Figure 4.20. The effect of WMA additives on SARA fractions (Kırıkkale Refinery)

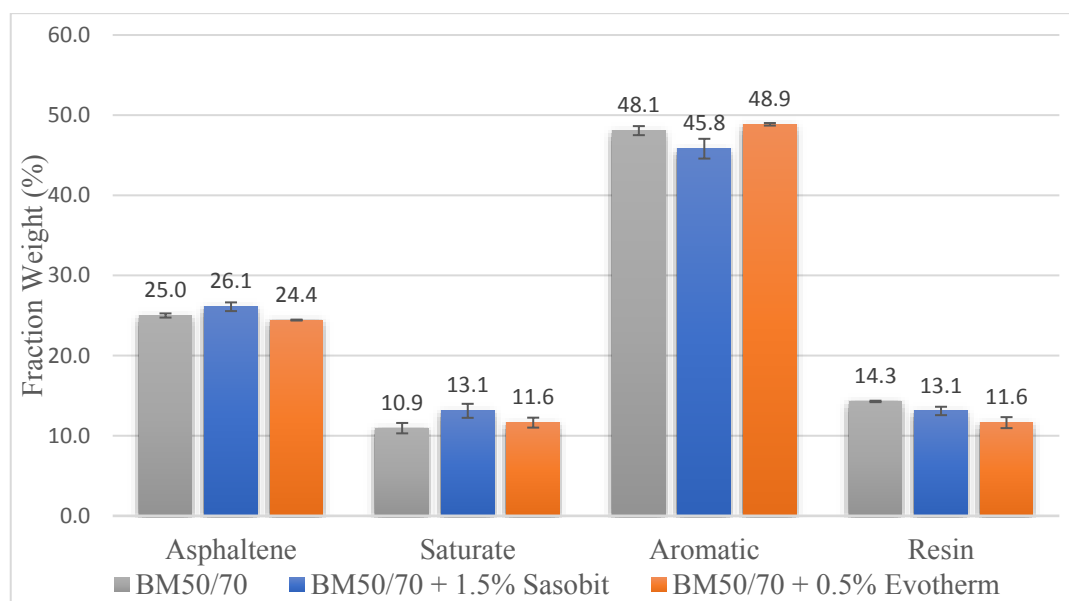


Figure 4.21. The effect of WMA additives on SARA fractions (Batman Refinery)

The physical properties of WMA additives (Sasobit and Evotherm) indicate that the fractions changing in tandem with the physical properties of the bituminous binder after adding WMA additives are asphaltene and aromatic fractions. Consequently, to comprehend the impact of WMA additives on the SARA fractions and physical properties of the bituminous binder, the key fractions to evaluate are asphaltene and aromatic fractions.

The viscosity of the asphalt binder is also influenced by the interaction of chemical molecules within the asphalt binder and its molecular weight (Redelius & Soenen, 2015). Studies indicate that viscosity increases as the asphaltene content within the asphalt binder increases (Dealy, 1979; Glover et al., 1987; Robertson, 2021). In this study, the viscosity of binders modified with Evotherm and Sasobit and unmodified binders are presented in Figure 4.18. Figure 4.19 shows that the viscosities of asphalt binders are in the same range after 150°C. Thus, comparisons of viscosities at 120°C, 130°C, and 140°C are more distinctive.

As seen in Figure 4.22, the bituminous binders with the highest viscosity values are BM50/70 and BM50/70 + 0.5% Evotherm, followed by BM50/70 + 1.5% Sasobit. The asphaltene contents of BM50/70 + 1.5% Sasobit, BM50/70, and BM50/70+0.5% Evotherm in a sequence are 26.1%, 25%, and 24.4%. Although BM50/70 + 1.5% Sasobit has the highest asphaltene ratio, it exhibits lower viscosity than BM50/70 and BM50/70 + 0.5% Evotherm binders. Similarly, as observed in Figure 4.15, when examining KK50/70 obtained from the Kırıkkale refinery and modified bituminous binders, KK50/70 and KK50/70 + 0.5% Evotherm have higher viscosity values than KK50/70 + 1.5% Sasobit. The asphaltene contents of KK50/70 + 1.5% Sasobit, KK50/70 and KK50/70+0.5% Evotherm are 19.1%, and 17.7%, in a sequence. Although KK50/70 + 1.5% Sasobit has the highest asphaltene ratio, it exhibits lower viscosity than KK50/70 and KK50/70 + 0.5% Evotherm binders. The viscosity values and asphaltene contents discussed are close; nonetheless, establishing a direct relationship between the asphaltene ratio and viscosity is not possible for modified asphalt binders.

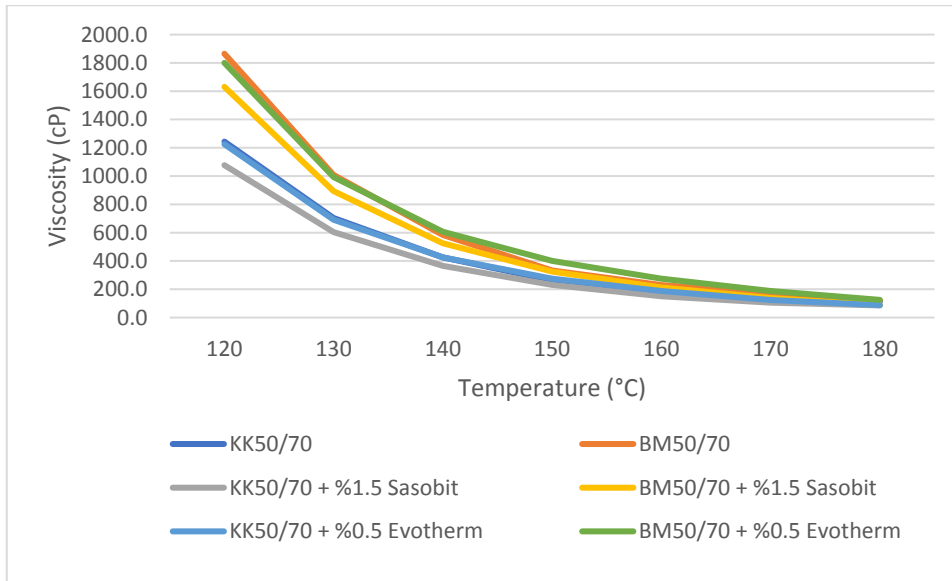


Figure 4.22. Viscosity and temperature graph of modified bituminous binders

4.2.3 Rheological Properties of Bituminous Binder with WMA Additive

Modification with WMA additives changes the rheological properties of the bituminous binders (Behnhood, 2020; Xiao et al., 2012; Zhang et al., 2015; Zhang et al., 2023). Although the binders are modified with the same WMA additives, refinery-based differences in their rheological properties exist. These variations in the true grades and short-term and long-term rheological properties of asphalt binders upon modification are analyzed in this section.

The changes in the high-temperature true grades and PG grades of asphalt binders modified with WMA additives are given in Table 4.4. The Sasobit additive increases the true grade for unaged bituminous binders, whereas the Evotherm additive slightly reduces the true grade. The true grade of the KK50/70 binder, which is 70°C (original), is increased to 74.5°C when modified with Sasobit and decreased to 69.10°C when modified with Evotherm. Similarly, the true grade of the BM50/70 binder, which is 74.8, increased to 76.6°C with Sasobit modification and decreased

to 71.2°C with Evotherm modification. Moreover, it is also observed that considering the KK50/70, modification with Sasobit results in an increase in the intermediate temperature true grades, whereas modification with Evotherm leads to a decrease in the intermediate true grade. On the other hand, it is observed that for the BM50/70 binder, while Sasobit addition also increases the intermediate temperature true grade, modification of Evotherm also increases slightly increases the true grade by 0.70°C. It should also be noted that in the literature, it is indicated that Evotherm does not influence the performance grade, which meets the findings of the study.

Table 4.4 True and performance grade (PG) of modified bituminous binders

Bituminous Binders	True Grades (°C)	Performance Grade (PG)
KK50/70	70.00	70
KK50/70+%1.5 Sasobit	74.50	70
KK50/70+%0.5 Evotherm	69.10	64
BM50/70	74.80	70
BM50/70+ %1.5 Sasobit	76.60	76
BM50/70+ %0.5 Evotherm	74.20	70
KK50/70 RTFO	74.40	70
KK50/70+%1.5 Sasobit (RTFO)	75.40	70
KK50/70+%0.5 Evotherm (RTFO)	71.20	70
BM50/70 RTFO	83.50	82
BM50/70+ %1.5 Sasobit (RTFO)	84.20	82
BM50/70+ %0.5 Evotherm (RTFO)	81.80	76
KK50/70 PAV	25.90	
KK50/70+%1.5 Sasobit (PAV)	27.40	
KK50/70+%0.5 Evotherm (PAV)	23.00	
BM50/70 PAV	21.00	
BM50/70+ %1.5 Sasobit (PAV)	24.50	
BM50/70+ %0.5 Evotherm (PAV)	21.70	

Table 4.5 presents the complex shear modulus, phase angle (δ), and $G^*/\sin\delta$ of unaged base and modified bituminous binders at intermediate and high temperatures. Accordingly, it is observed that the Sasobit additive raises the complex shear

modulus of bituminous binders at high and intermediate temperatures for both BM50/70 and KK50/70 binders. Meanwhile, it is measured that Evotherm only increases the binder's complex shear modulus at intermediate temperatures. It should also be noted that the complex shear modulus of the binder modified with Evotherm is lower than the ones modified with Sasobit at high and intermediate temperatures. Additionally, the modified BM50/70 binders exhibit higher complex shear modulus values than the modified KK50/70 binders, in line with the base binder properties.

Evaluating the phase angle (δ) of unaged bituminous binders, it is evident that the addition of Sasobit contributes to a reduction in the phase angle (δ). Modified binders incorporating Sasobit demonstrate the lowest phase angles (δ) among both KK50/70 and BM50/70 binders, compared to unmodified binders and those modified with Evotherm. Conversely, Evotherm elevates phase angle (δ). Modification of the KK50/70 binder with Evotherm results in the highest phase angle (δ) for both intermediate and high temperatures. However, in the case of the BM50/70 binder, the impact of Evotherm on the phase angle (δ) is only visible at high temperatures, and Evotherm shows no effect on the phase angle (δ) at intermediate temperatures. Therefore, the Evotherm additive increases the phase angle values of bituminous binders at high temperatures, causing a more viscous deformation behavior in the binder. Furthermore, the Sasobit additive decreases the phase angle values of the binder at both high and intermediate temperatures, showing a more elastic deformation behavior. Additionally, the modified binders obtained from the Kırıkkale refinery's phase angle value is higher than the modified bituminous binders obtained from the Batman refinery. However, complex shear modulus and phase angle should be considered together.

The rutting resistance of KK50/70 and BM50/70 binders modified with Sasobit is the highest in intermediate (34-40°C) and high temperatures (64-70°C). Thus, Sasobit enhances the rutting resistance of the bituminous binder at both intermediate and high temperatures (West et al., 2013). Meanwhile, it is observed that Evotherm is only effective at intermediate temperatures since the base binders (KK50/70 and BM50/70) have more rutting resistance than Evotherm-modified binders at high

temperatures. Hence, Sasobit enhances the rutting resistance of the bituminous binder in both intermediate and high temperatures, and Evotherm additive exhibits effectiveness in terms of rutting resistance only at intermediate temperatures.

Table 4.5 Rheological properties of unaged modified bituminous binders

f=10 Hz		Temperature (°C)			
Unaged Bituminous Binder		34	40	64	70
KK50/70 + 0.5% Evotherm	G*, Pa	656800	297100	10640	5156
	Phase Angle (δ)	65.0	70.4	82.7	84.2
	G*/sin δ , kPa	724.6	315.4	10.7	5.2
KK50/70	G*, Pa	728600	290300	10740	5498
	Phase Angle (δ)	63.7	69.6	82.0	83.6
	G*/sin δ , kPa	812.8	309.6	10.8	5.5
KK50/70 + %1.5 Sasobit	G*, Pa	1214000	571800	18390	8954
	Phase Angle (δ)	57.1	64.0	78.7	80.6
	G*/sin δ , kPa	1445.9	636.0	18.8	9.1
BM50/70 + %0.5 Evotherm	G*, Pa	553800	282700	15770	8475
	Phase Angle (δ)	56.1	59.6	73.0	76.3
	G*/sin δ , kPa	667.6	327.8	16.5	8.7
BM50/70	G*, Pa	539400	279100	16150	8628
	Phase Angle (δ)	56.4	59.9	72.3	75.1
	G*/sin δ , kPa	648.0	322.7	17.0	8.9
BM50/70 + %1.5 Sasobit	G*, Pa	847700	446000	22160	10480
	Phase Angle (δ)	49.8	54.9	70.5	74.0
	G*/sin δ , kPa	1110.0	545.5	23.5	10.9

Table 4.6 presents both and modified bituminous binders' complex shear modulus (G^*), phase angle, and $G^*/\sin(\delta)$ values after short-term aging. After short-term aging, the highest complex shear modulus is also observed in the Sasobit-modified binders, followed by base binders (KK 50/70 and BM50/70). Subsequently, the modified binders with Evotherm exhibit the lowest complex shear modulus. From Table 4.6, it can also be observed that the phase angle values of binders modified with Evotherm are higher than the base and Sasobit modified binders at high and intermediate temperatures. The sequence from the highest to lowest phase angles can be listed as Evotherm modified, base, and the Sasobit-modified binder. This trend is valid for both binders obtained from Kırıkkale and Batman refineries. Consequently, binders modified with Evotherm exhibit a more viscous deformation behavior after short-term aging, whereas those modified with Sasobit demonstrate elastic deformation behavior. To sum up, the rutting resistance ($G^*/\sin(\delta)$) of bituminous binders after short-term aging reveals that binders modified with Sasobit exhibit higher rutting resistance compared to base binders at temperatures in the range of 34-70°C. Meanwhile, binders modified with Evotherm reveal the lowest resistance.

Table 4.6 Rheological properties of short-term aged modified bituminous binders

f=10 Hz		Temperature (°C)			
RTFO Aged Bituminous Binder		34	40	64	70
KK50/70 + %1.5 Sasobit RTFO	G*, Pa	2092000	1074000	44160	20540
	Phase Angle (δ)	45.5	53.0	72.3	75.2
	$G^*/\sin\delta$, kPa	2932.5	1344.4	46.4	21.2
Kırıkkale50/70 RTFO	G*, Pa	1751000	895800	38280	18650
	Phase Angle (δ)	49.4	55.9	72.8	76.0
	$G^*/\sin\delta$, kPa	2305.1	1082.3	40.1	19.2
KK50/70 + 0.5% Evotherm RTFO	G*, Pa	1344000	652900	27450	13260
	Phase Angle (δ)	53.8	59.9	75.7	78.5
	$G^*/\sin\delta$, kPa	1665.5	754.5	28.3	13.5
	G*, Pa	1795000	994300	74900	39220

Table 4.6 (cont'd)

BM50/70 + %1.5 Sasobit RTFO	Phase Angle (δ)	39.5	44.7	58.0	61.2
	$G^*/\sin\delta$, kPa	2822.0	1414.3	88.3	44.7
Batman50/70 RTFO	G^* , Pa	1454000	806500	62320	34640
	Phase Angle (δ)	43.3	47.3	59.5	62.0
	$G^*/\sin\delta$, kPa	2118.9	1097.8	72.3	39.2
BM50/70 + %0.5 Evotherm RTFO	G^* , Pa	1303000	719000	55270	30540
	Phase Angle (δ)	44.5	48.6	60.6	63.7
	$G^*/\sin\delta$, kPa	1860.3	959.1	63.4	34.1

The changes in the modified and base bituminous binders after long-term aging at intermediate and high temperatures are also given in Table 4.7. When examining the complex shear modulus of the binders obtained from the Kırıkkale refinery at 34°C, the highest complex shear modulus belongs to KK50/70+ 1.5% Sasobit binder, followed by the complex shear modulus of KK50/70, which is higher than the complex shear modulus of KK50/70 + 0.5% Evotherm binder. At 40°C, again, the complex shear modulus of K50/70 + 1.5% Sasobit binder is the highest, followed by KK50/70 + 0.5% Evotherm binder and then base binder. At high temperatures (64-70°C), the binder with the highest complex shear modulus is the Sasobit-modified binder, followed by the unmodified (KK50/70) binder, and then the Evotherm-modified binder. Binders from the Batman refinery exhibit the same pattern at high and intermediate temperatures. Assessing the phase angle values for binders from the Kırıkkale refinery, the binder with the highest phase angle is the Evotherm-modified binder. At the same time, the one with the lowest is the Sasobit-modified binder. Hence, the Evotherm-modified binders exhibit more viscous deformation behavior at high and intermediate temperatures. For the binders from the Batman refinery, the Evotherm-modified binder demonstrates the highest phase angle value at high and intermediate temperatures. Comparatively, the phase angle values of BM50/70 PAV and BM50/70 + 1.5% Sasobit binders appear remarkably similar. In summary, the Sasobit-modified and unmodified binders display behavior closely resembling each other yet relatively more elastic deformation behavior than the

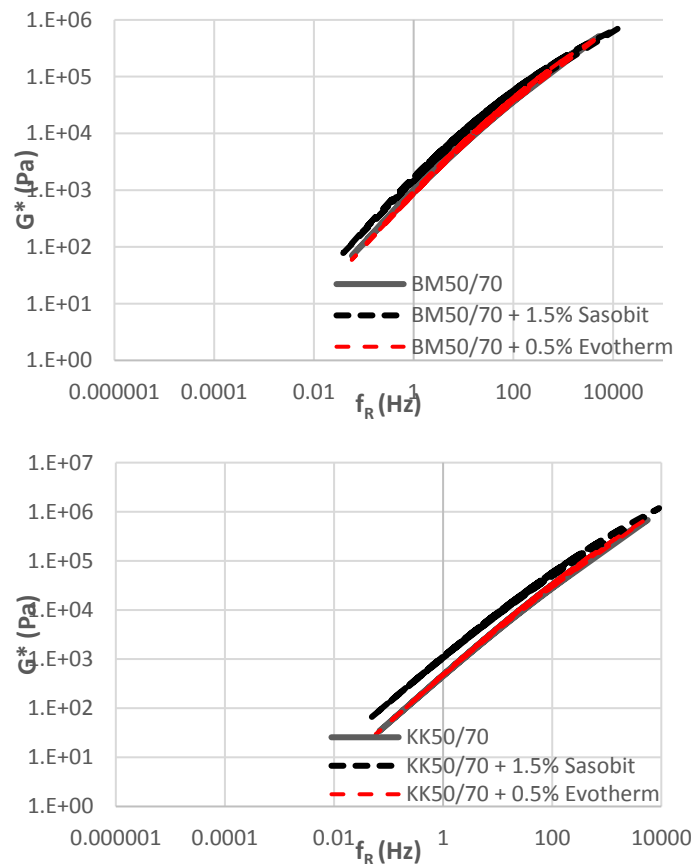
Evotherm-modified binder. For the Kırıkkale refinery's products, at intermediate temperatures, the Sasobit-modified binder displays the highest rutting resistance, followed by the unmodified binder, and then the Evotherm-modified binder, which demonstrates the lowest rutting resistance. Consequently, the change in the rheological parameters of binders obtained from Batman and Kırıkkale refineries, along with WMA additives, is the same.

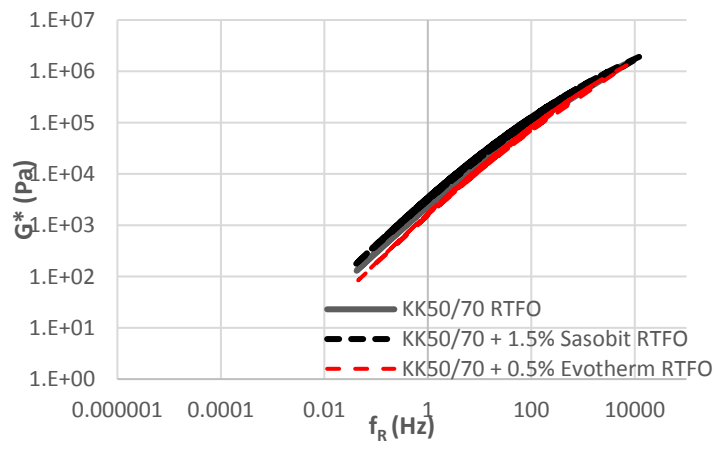
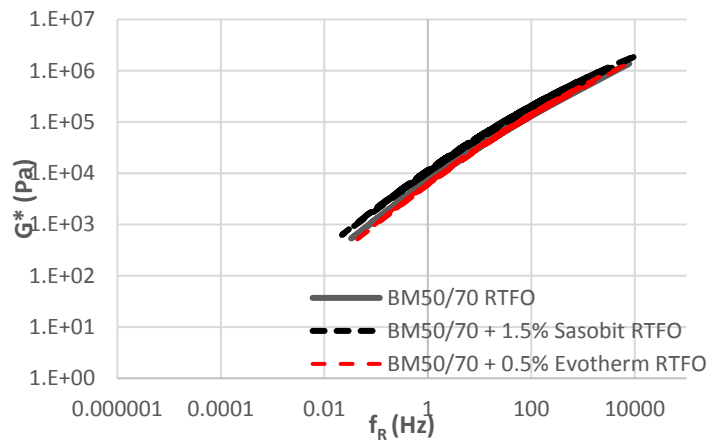
Table 4.7 Rheological properties of long-term aged modified bituminous binders

f=10 Hz		Temperature (°C)			
Long-Term Aged Bituminous Binder		34	40	64	70
KK50/70 + %1.5 Sasobit PAV	G*, Pa	7543000	3835000	252900	136200
	Phase Angle (δ)	40.2	43.7	57.9	61.6
	G*/sin δ , kPa	10874.1	4949.0	299.0	189.0
KK50/70 PAV	G*, Pa	7277000	3585000	207700	103600
	Phase Angle (δ)	42.0	46.4	61.1	66.5
	G*/sin δ , kPa	10873.2	4948.0	237.3	112.9
KK50/70 + 0.5% Evotherm PAV	G*, Pa	5599000	2669000	138200	68030
	Phase Angle (δ)	44.4	49.3	65.4	70.5
	G*/sin δ , kPa	7999.6	3518.4	152.0	72.2
BM50/70 + %1.5 Sasobit PAV	G*, Pa	6970000	3910000	456000	273000
	Phase Angle (δ)	34.3	36.8	45.3	46.8
	G*/sin δ , kPa	12378.1	6530.3	641.8	374.4
BM50/70 PAV	G*, Pa	5540000	3070000	373700	228100
	Phase Angle (δ)	34.9	37.2	44.8	46.0
	G*/sin δ , kPa	9682.8	5077.7	530.3	316.9
BM50/70 + %0.5 Evotherm PAV	G*, Pa	6738000	3532000	242600	130100
	Phase Angle (δ)	40.0	43.7	58.4	61.5
	G*/sin δ , kPa	8751.1	4408.7	381.9	215.1

Therefore, WMA additives show some variations in bituminous binders based on the binder source, but mostly, WMA additives exhibit similar effects on the binders. Moreover, master curves are constructed to examine alterations in the rheological

parameters of modified binders with increasing frequency and temperature. Figure 4.23 demonstrates the changes in the complex shear modulus of bituminous binders when modified with Evotherm and Sasobit additives compared to the base binder after aging. The addition of Sasobit to the BM50/70 binder shows a slight increase in complex shear modulus, while Evotherm exhibits a marginal decrease. Notably, the Sasobit additive increases the complex shear modulus for the KK50/70 binder, particularly at lower frequencies. Following a short-term aging process, similar alterations in complex shear modulus are observed for KK50/70 and BM50/70 binders with Sasobit and Evotherm additives. Evotherm decreases the complex shear modulus, whereas Sasobit increases it. After a long-term aging process, Evotherm significantly reduces the low-frequency complex shear modulus of the BM50/70 binder, whereas Sasobit marginally increases it. Consequently, in the case of the KK50/70 and BM50/70 binder, Evotherm decreases the complex shear modulus whereas Sasobit demonstrates an increase.





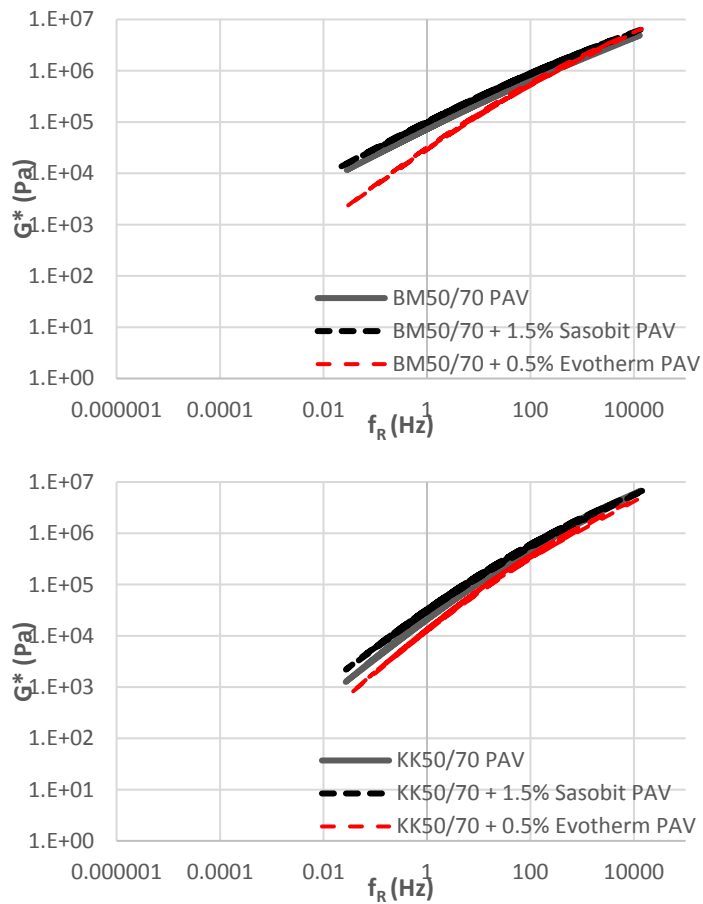
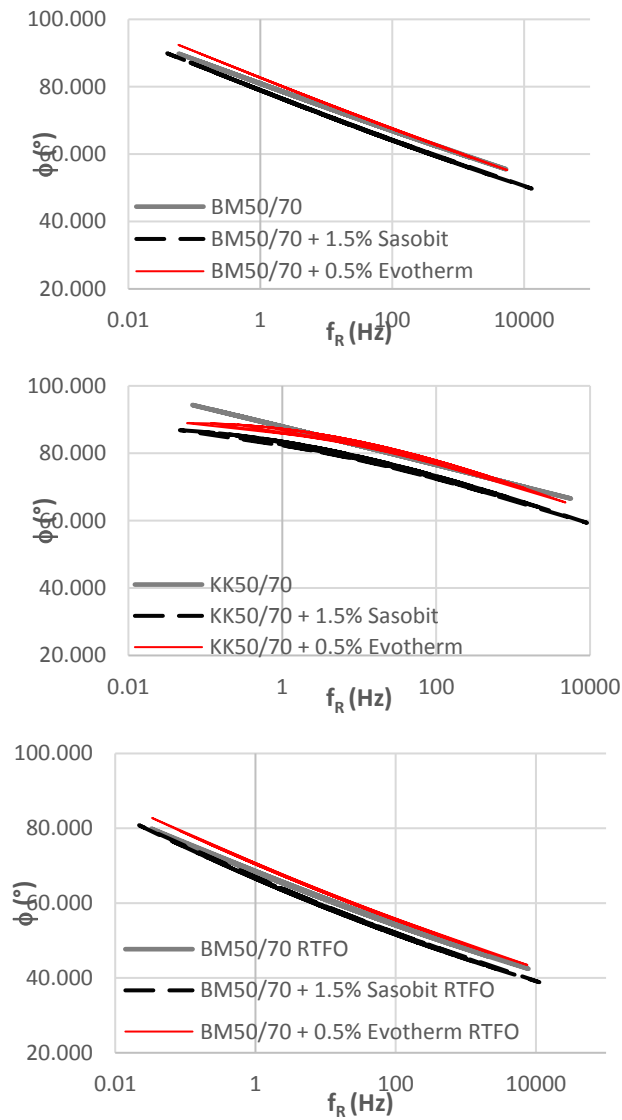


Figure 4.23. Complex shear modulus vs frequency master curve of modified bituminous binders

In Figure 4.24, the changes in the phase angles of bituminous binders modified with WMA additives with aging are presented. For the BM50/70 binder, an increase in phase angle is observed with the addition of Evotherm and a decrease with Sasobit. Particularly after a long-term aging process, the phase angle of the Evotherm-modified BM50/70 binder significantly increases. The significant increase in the phase angle of the BM50/70 binder due to Evotherm is also illustrated in Table 4.7. However, the Evotherm additive does not exert the same level of effect on the KK50/70 binder. For the KK50/70 binder, Sasobit slightly reduces the binder's phase angle. However, the Evotherm additive decreases the binder's phase angle, especially

in the unaged state and at low frequencies, with its effect becoming more pronounced after both short-term and long-term aging processes.



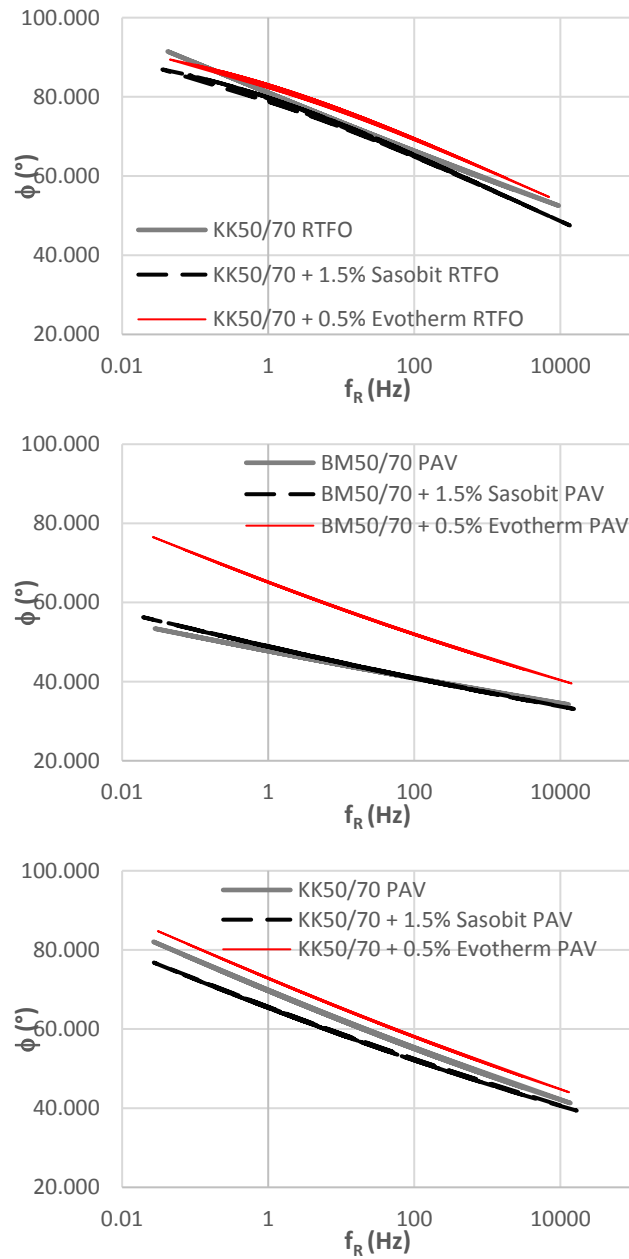


Figure 4.24. Phase angle vs frequency master curve of modified bituminous binders

4.2.4 Relationship Between Rheological Properties and SARA Fractions of Modified Bituminous Binders

The composition of SARA fractions changes with the aging of the modified bituminous binders. Thus, this section analyzes the relationship between SARA

fractions and the rheological properties of modified bituminous binders. As stated in Section 4.1.4, the aging process of unmodified bituminous binders increases the asphaltene fraction and decreases the aromatic fraction while the resin and saturate fraction slightly change. However, no research has addressed these variations in each SARA fraction of modified bituminous binder with WMA additive after aging.

4.2.4.1 The Changes in SARA Fractions of Modified Bituminous Binders After Short-Term (RTFO) Aging

The influence of Sasobit and Evotherm additive on the SARA fractions due to short-term aging will be discussed in this section. Figure 4.25 and Figure 4.26 show the change in SARA fractions of modified KK50/70 and BM50/70 binders after short-term aging. After subjecting the bituminous binders modified with Sasobit and Evotherm to short-term aging, the SARA fractions differ from those of the base binders.

The Sasobit-modified KK50/70 binder exhibits a 0.3% increase in the asphaltene fraction and a 0.1% decrease in the aromatic fraction, which may be negligible. However, there is a 1.4% increase in the saturate fraction and a 1.8% decrease in the resin fraction. Similarly, as given in Figure 4.26, the asphaltene and saturate fractions of the Sasobit-modified BM50/70 binder are 1.3% and 3.9% higher than the base binder, respectively. On the contrary, the aromatic and resin fractions decreased by 1.4% and 1.8%, respectively, with respect to base binder. Thus, the influence of Sasobit addition is particularly noticeable in the saturate and resin fractions in short-term aging. The increase in the saturate fraction, known for softening the bituminous binder, and the decrease in the resin fraction, known for hardening it, indicate that the binder is less affected by short-term aging than the unmodified binder. In summary, while Sasobit's effects on both base binders, such as increase in asphaltene and saturate fractions, and decrease in resin and aromatic fractions, are similar, the magnitude of these effects differs. Hence, it can be concluded that the change in SARA fractions depends on the binder source.

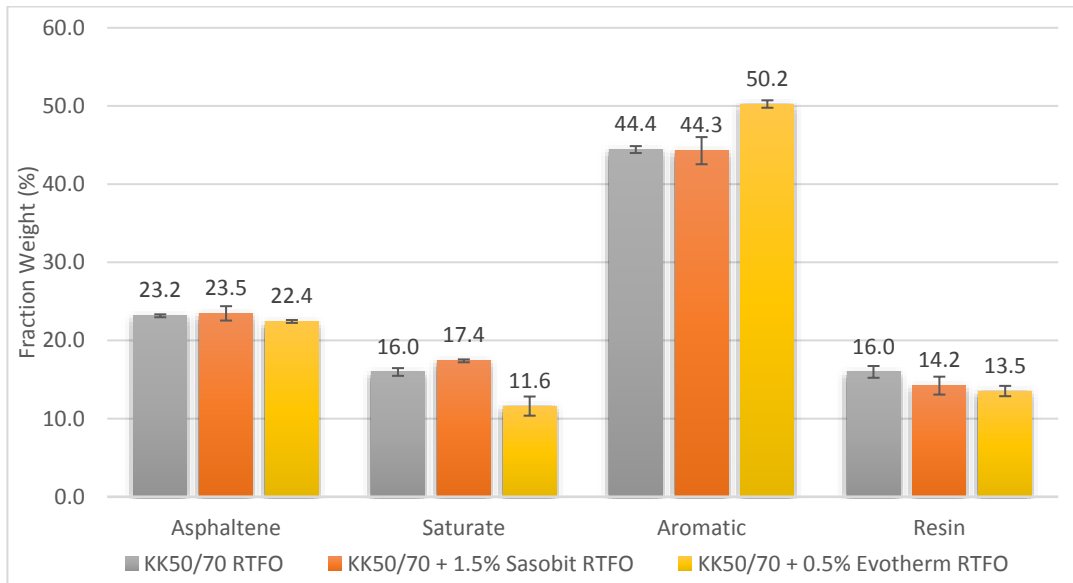


Figure 4.25. The change in SARA fractions of modified KK50/70 binder after Short-Term Aging

It is also observed that the Evotherm-modified KK50/70 binder exhibits a decrease in the asphaltene, saturate, and resin fractions, 0.8%, 4.4% and 2.5%, respectively. On the contrary, the aromatic fraction increases by 5.8%, which enhances the flexibility of the bituminous binder. Moreover, when Figure 4.26 is analyzed, it is determined that the Evotherm-modified BM50/70 binder shows a 1% increase in the asphaltene fraction and a substantial 5.6% rise in the aromatic fraction, accompanied by a 2% decrease in the saturate fraction and a 2.5% reduction in the resin fraction. These significant variations in aromatic fractions of both binders can be attributed to the softening effect of the Evotherm additive. Additionally, the expected resistance to oxidation, indicated by the decrease in the saturate fraction, seems to have been affected by oxidation. Furthermore, comparing the SARA fractions of the binders, it is evident that the Evotherm additive has caused a more significant alteration in the SARA composition of binders than Sasobit in the short-term aging process.

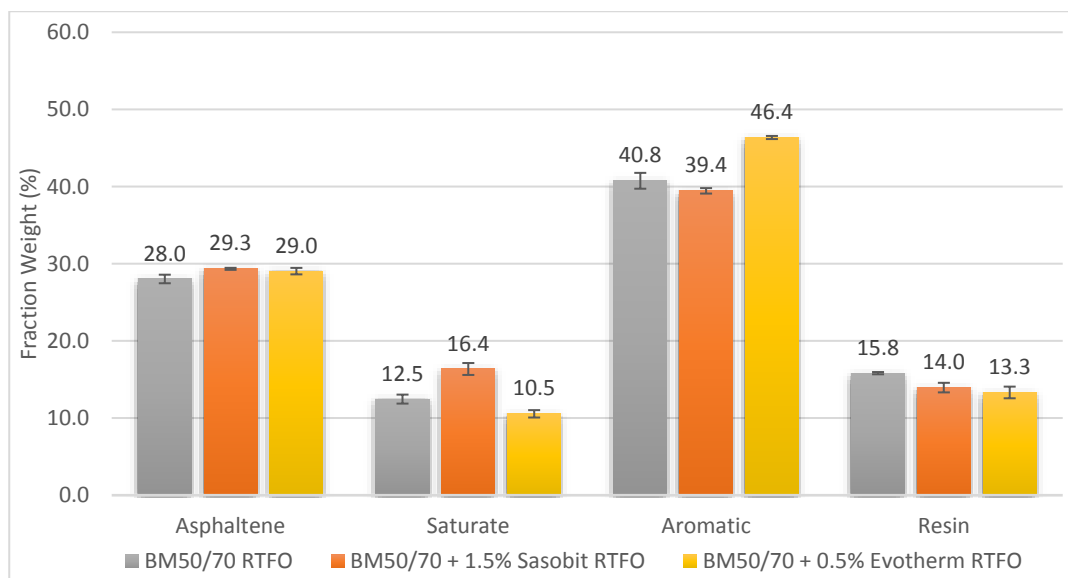


Figure 4.26. The change in SARA fractions of modified BM50/70 binder after Short-Term Aging

4.2.4.2 The Changes in SARA Fractions of Modified Bituminous Binders After Long-Term Aging (PAV)

Long-term aging exhibits more changes in the SARA fractions of bituminous binders than short-term aging. Figure 4.27 and Figure 4.28 show the changes in the SARA fractions of the base binders (KK50/70 and BM50/70) and binders modified with Sasobit and Evotherm after long-term aging.

The Sasobit-modified KK50/70 binder shows a 0.6% increase in the asphaltene fraction and a 0.5% decrease in the saturate fraction. Moreover, the aromatic fraction has 3.6% increase compared to the unmodified binder, whereas the resin fraction is reduced by 3.6% as compared to base binder. On the other hand, following the long-term aging process, the Sasobit-modified BM50/70 binder exhibits a 3.1% reduction in asphaltene content and a 2.3% increase in saturate fraction. As it can be reported the variations in asphaltene and saturate fractions are opposite for KK50/70 and BM50/70. On the other hand, the variations in resin and aromatic fractions are

similar. It is measured as a 3% reduction in resin fraction and a 4.7% increase in aromatic fraction. Thus, the binder source highly influences the modification with Sasobit.

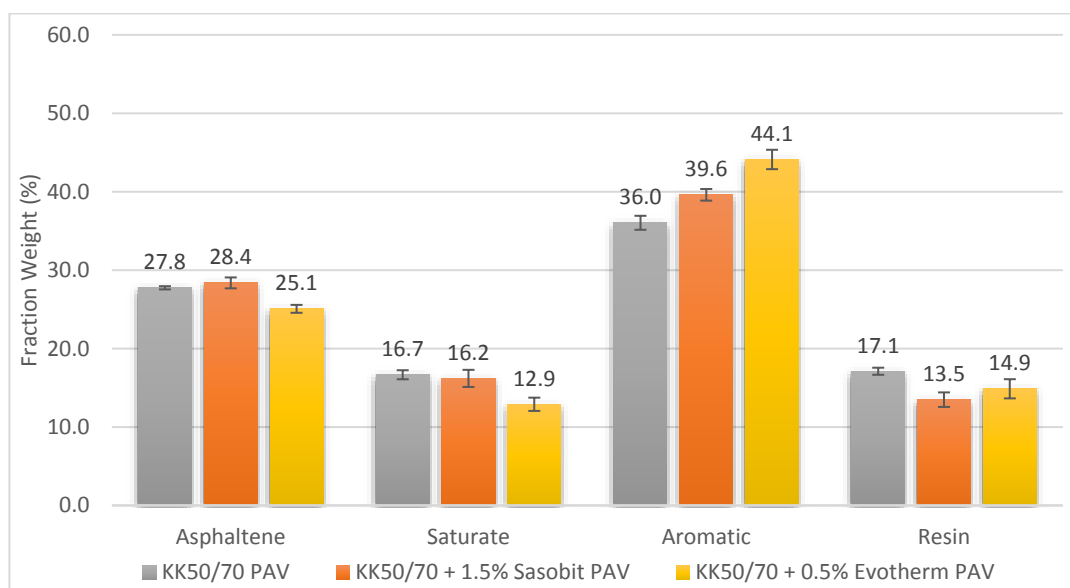


Figure 4.27. The changes in SARA fractions of modified KK50/70 binder after long-term aging

As given in Figure 4.27, the effect of the long-term aging process on the Evotherm-modified KK50/70 binder is that asphaltene, saturate, and resin fractions are reduced by 2.7%, 3.8%, and 2.2%, respectively, whereas the aromatic fraction is increased by 8.1% with respect to the base binder. Furthermore, the long-term aging effect of the Evotherm additive has been observed on BM50/70 binder as follows: the asphaltene and resin fractions are 2.9% and 4.4% lower than the base, whereas the saturate and aromatic fractions increase by 1.4% and 6.5%, respectively. The difference in saturate fractions indicates the differences in the resistance to oxidation, which depends on the binder source.

After the long-term aging process, although there are differences in behaviors, it can still be generalized that the effects on the binder from Sasobit and Evotherm reveal

a decrease in the total asphaltene and resin fractions. Simultaneously, it can be generalized that there is an increase in the saturate and aromatic fractions. Considering the SARA fractions following the long-term aging process, it is obvious that, along with additives, the bituminous binders harden less compared to the unmodified binder. Moreover, the aromatic fraction significantly increases in each modified binder subjected to long-term aging. This escalation signifies the increasing flexibility of the modified binders compared to the unmodified bituminous binder.

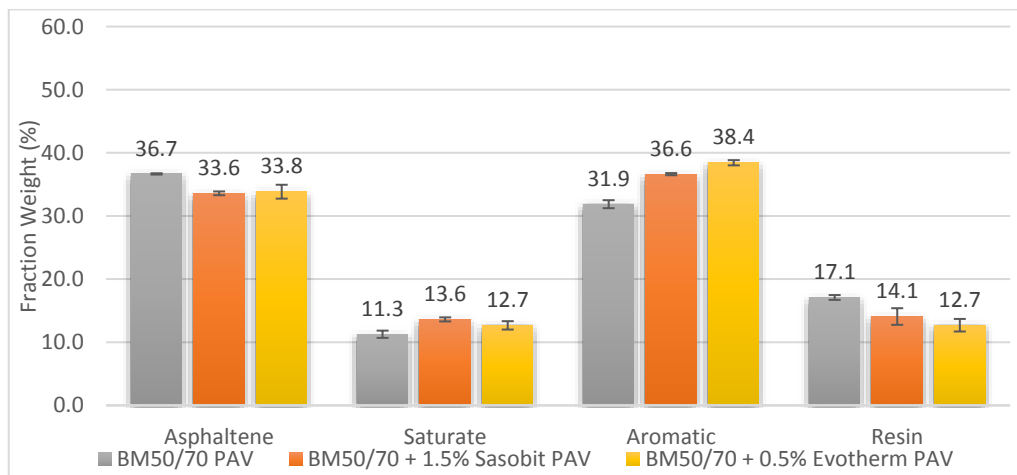


Figure 4.28. The change in SARA fractions of modified BM50/70 binder after long-term aging

4.2.4.3 Relationship Between Asphaltene Fraction and Rheological Properties of Modified Bituminous Binders

Bituminous binders modified with Sasobit and Evotharm were subjected to DSR tests to determine their rheological properties at intermediate and high temperatures. Table 4.8 illustrates the correlation between the asphaltene content of modified bituminous binders from the Kırıkkale refinery and their corresponding high and

intermediate-temperature true grades. It is known that as bituminous binders age, both their true grades and asphaltene fractions increase. Examining modified bituminous binders derived from Kırıkkale refinery, an increase in asphaltene corresponds to an increase in intermediate and high-temperature true grade.

Table 4.8 Asphaltene content and true grade of modified binders from Kırıkkale refinery

Bituminous Binders	Asphaltene (%)	True Grades (°C)
KK50/70+%0.5 Evotherm	17.7	69.10
KK50/70	18.4	70.00
KK50/70+%1.5 Sasobit	19.1	74.50
KK50/70+%0.5 Evotherm (RTFO)	22.7	71.20
KK50/70 RTFO	23.4	74.40
KK50/70+%1.5 Sasobit (RTFO)	23.5	75.40
KK50/70+%0.5 Evotherm (PAV)	25.1	23.00
KK50/70 PAV	27.8	25.90
KK50/70+%1.5 Sasobit (PAV)	28.6	27.40

Table 4.9 shows the relationship between the true grade and asphaltene content of base and modified bituminous binders obtained from the Batman refinery. A relationship exists between the asphaltene content and true grade values of bituminous binders from the Batman refinery in their unaged state. However, this relationship is not observed in both short-term and long-term aged conditions. In other words, there is no relationship between the asphaltene content and true grades of modified bituminous binders obtained from the Batman refinery when subjected to aging. This difference is related to the binder source.

Table 4.9 Asphaltene content and true grade of modified binders from Batman refinery

Bituminous Binders	Asphaltene (%)	True Grades (°C)
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Table 4.9 (cont'd)

BM50/70+ %0.5 Evotherm	24.4	74.20
BM50/70	25.0	74.80
BM50/70+ %1.5 Sasobit	26.1	76.60
BM50/70 RTFO	28.0	82.8
BM50/70+ %0.5 Evotherm (RTFO)	29.0	82.2
BM50/70+ %1.5 Sasobit (RTFO)	29.3	85
BM50/70+ %1.5 Sasobit (PAV)	33.6	24.50
BM50/70+ %0.5 Evotherm (PAV)	33.8	25
BM50/70 PAV	36.7	20.2

Moreover, Table 4.10 shows the Sasobit-modified KK50/70, the Evotherm-modified KK50/70 binder and base bituminous binder's rheological properties at high temperatures. As the bituminous binder ages, there is an increase in the asphaltene percentage and the complex shear modulus while the phase angle decreases. The asphaltene percentage in the KK50/70 binder modified with Sasobit is higher compared to the base binder and the percentage of asphaltene content is higher than the binder modified with Evotherm. At intermediate temperatures, the Evotherm and Sasobit modified binders' asphaltene fraction and complex shear modulus values also increase with aging and the phase angle value also decreases (See Appendix).

Table 4.10 High-Temperature Properties of Modified Binders Obtained Kırıkkale Refinery

Bituminous Binders	Asphaltene (%)	T=64°C, f=10Hz			T=70°C, f=10Hz		
		G* (Pa)	Phase Angle (δ)	G*/sinδ, kPa	G* (Pa)	Phase Angle (δ)	G*/sinδ, kPa
KK50/70 + 0.5% Evotherm	17.7	10640	82.7	11	5156	84.2	5
KK50/70	18.4	10740	82.0	11	5498	83.6	6
KK50/70 + 1.5% Sasobit	19.1	18390	78.7	19	8954	80.6	9
KK50/70 + 0.5%	22.7	27450	75.7	28	13260	78.5	14

Table 4.10 (cont'd)

Evotherm RTFO							
KK50/70 RTFO	23.4	38280	72.8	40	18650	76.0	19
KK50/70 + 1.5% Sasobit RTFO	23.5	44160	72.3	46	20540	75.2	21
KK50/70 + 0.5% Evotherm PAV	25.1	138200	65.4	152	68030	70.5	72
KK50/70 PAV	27.8	207700.0	61.1	237	103600	66.5	113
KK50/70 + 1.5% Sasobit PAV	28.6	252900	57.9	299	136200	61.6	189

In Table 4.11, the changes in the complex shear modulus and phase angle values of base and modified bituminous binders at high temperatures due to short-term and long-term aging are presented for Batman binders. In the unaged state of binders, as the asphaltene fraction increases, the complex shear modulus value rises and the phase angle value decreases, consequently, increases the rutting resistance. However, no relationship is observed between the asphaltene content and complex shear modulus or phase angle values of binders after short-term and long-term aging. For instance, the asphaltene content of Evotherm modified BM50/70 binder is higher than BM50/70 RTFO aged binder, but the complex shear modulus value is lower. After long-term aging, the Sasobit modified BM50/70 binder has the highest rutting resistance while having the lowest asphaltene content.

Table 4.11 High-Temperature Properties of Modified Binders Obtained from Batman Refinery

Bituminous Binders	Asphaltene (%)	T=64°C, f=10Hz			T=70°C, f=10Hz		
		G* (Pa)	Phase Angle (δ)	G*/sin δ , kPa	G* (Pa)	Phase Angle (δ)	G*/sin δ , kPa

Table 4.11 (cont'd)

BM50/70 + 0.5% Evotherm	24.4	15770	73.0	16	8475	76.3	9
BM50/70	25.0	16150	72.3	17	8628	75.1	9
BM50/70 + 1.5% Sasobit	26.1	22160	70.5	24	10480	74.0	11
BM50/70 RTFO	28.0	62320	59.5	72	34640	62.0	39
BM50/70 + 0.5% Evotherm RTFO	29.0	55270	60.6	63	30540	63.7	34
BM50/70 + 1.5% Sasobit RTFO	29.3	85980	58.0	101	43900	61.3	45
BM50/70 + 1.5% Sasobit PAV	33.6	45600 0	45.3	642	27300 0	46.8	374
BM50/70 + 0.5% Evotherm PAV	33.8	24260 0	58.4	285	13010 0	61.5	396
BM50/70 PAV	36.7	34760 0	44.0	500	21620 0	45.1	259

In addition, no relationship between asphaltene content and rheological properties at intermediate temperature is observed. For instance, although the asphaltene content of the BM50/70 binder is higher than that of the Evotherm modified binder, the complex modulus value is lower. Similarly, after short-term and long-term aging processes, there is no relationship between the asphaltene content of binders from the Batman refinery and their rheological parameters (see Appendix). Thus, it is hard to build a direct relation between asphaltene content and rheology.

4.2.5 Gaestel Index (I_c) of Modified Bituminous Binders

The Gaestel Indices of modified bituminous binders have changed along with their SARA fractions. As indicated in the literature, the Gaestel Index is considered stable between 0.22 and 0.5. However, all base binders used in this study have indices above 0.5, indicating instability and hardness of the binder (See section 3.5.8). With the WMA additives, the physical properties of the bituminous binder have altered. It

has already been proven that Sasobit additive contributes to the hardening of the bituminous binder, while Evotherm additive softens it from physical properties. Figure 4.29 illustrates the variation in Gaestel Indices of modified binders. Sasobit additive increases the Gaestel Index, indicating further hardening of the binder. Conversely, with the addition of Evotherm, the Gaestel Index decreased, stabilizing the previously unstable unmodified KK50/70 binder and exhibiting gel-type behavior. However, unlike the Evotherm-modified KK50/70 binder, the Gaestel Index of the Evotherm-modified BM50/70 binder did not decrease; instead, it showed a slight increase. Additionally, the Gaestel index of binders obtained from the Batman refinery surpasses that of those obtained from the Kırıkkale refinery. Upon examination of WMA additive-modified binders, it is evident that binders obtained from the Batman refinery demonstrate a more pronounced variation in their Gaestel indexes. An increase in the Gaestel index indicates a transition to a more unstable microstructure of the bituminous binder. Therefore, binders obtained from the Batman refinery are more unstable compared to those obtained from the Kırıkkale refinery.

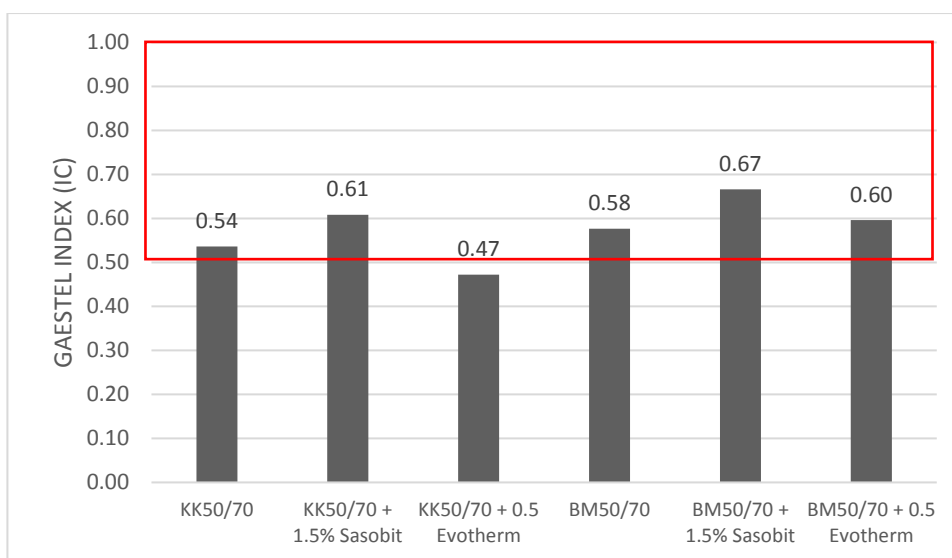


Figure 4.29. Gaestel Index of Unmodified and Modified Bituminous Binders

Figure 4.30 and Figure 4.31 display the variation in Gaestel indices of modified bituminous binders subjected to short-term and long-term aging. As a physical characteristic, bituminous binders tend to harden with aging. This hardening is due to the aging of modified bituminous binders. The addition of Sasobit has a more pronounced effect on increasing the Gaestel index than Evotherm for KK50/70 binders. In Figure 4.30, when the Sasobit-modified KK50/70 binder is exposed to long-term aging, a significant increase in the Gaestel index is observed, while the Evotherm-modified KK50/70 does not show such a drastic increase. Similarly, the Sasobit-modified BM50/70 binder exhibits the highest Gaestel index (See Figure 4.31). However, the Evotherm-modified BM50/70 binder substantially increases after short-term aging. While the asphaltene content of BM50/70 + 0.5% Evotherm PAV binder is 33.8%, the asphaltene content of BM50/70 + 0.5% Sasobit binder is 33.6%, indicating a close relationship between their Gaestel indices and asphaltene ratios.

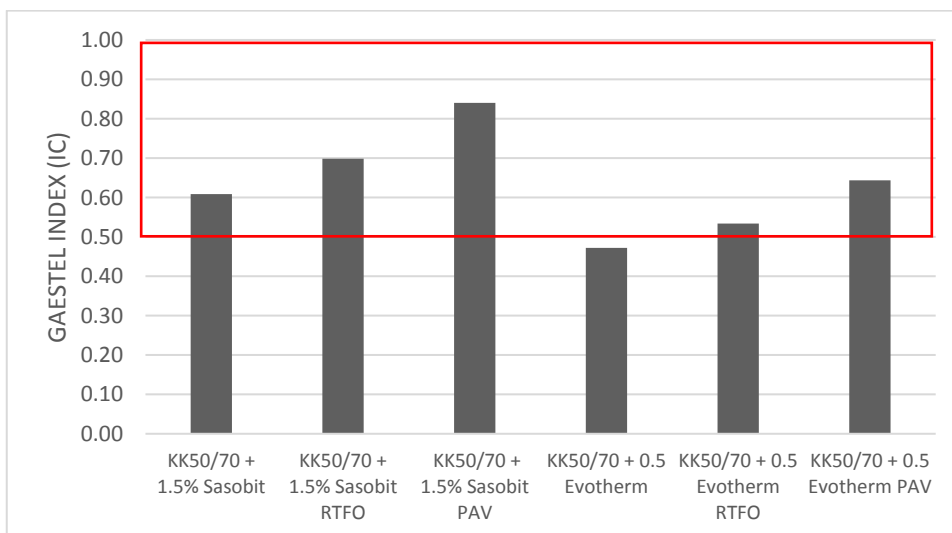


Figure 4.30. Gaestel Indices of modified and aged KK50/70 binder

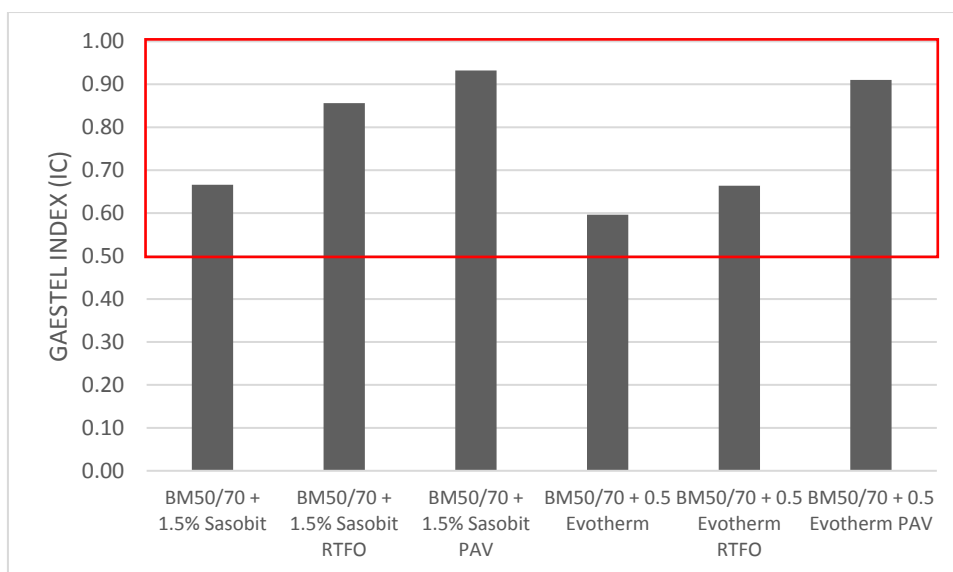


Figure 4.31. Gaestel Indices of modified and aged BM50/70 binder

4.2.6 FTIR Analysis Results of Modified Bituminous Binders

Upon modification with Evotherm and Sasobit, the changes in functional groups are evident. The FTIR spectra of KK50/70 modified with WMA additives are given in Figure 4.32. Upon reviewing the spectrum in Figure 4.32, it is evident that within the 1800-500 cm^{-1} wavenumber range, the intensity of the unmodified binder surpasses that of the Evotherm and Sasobit-modified binders. Subsequently, the Sasobit-modified binder displays a higher intensity compared to the Evotherm-modified binder, which demonstrates the lowest intensity among the observed binders. Moreover, the WMA additives do not create a new peak in the spectrum.

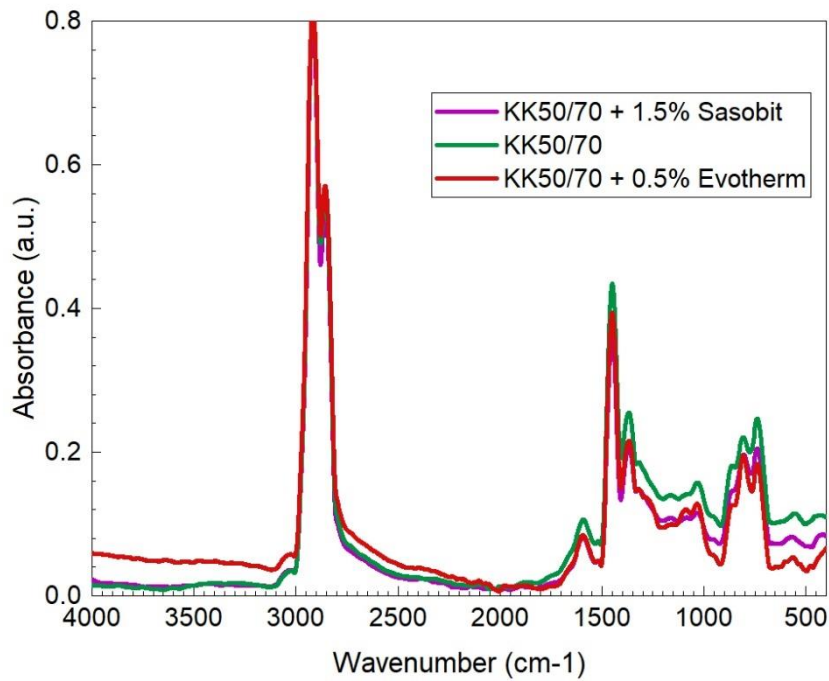


Figure 4.32. FTIR spectra of modified bituminous binder obtained from Kırıkkale refinery

Similarly, Figure 4.33 shows the changes in the FTIR spectra of the BM50/70 binder when modified with Sasobit and Evotherm. It is noticed that the spectra of the modified binders and the unmodified binder are similar within the approximate wavenumber range of 3000-1300 cm^{-1} . The intensity of the binders' spectra has changed within the wavenumber range of 500-1300 cm^{-1} . It is observed that the intensity of the Sasobit-modified binder is the highest, while the unmodified binder has the lowest intensity.

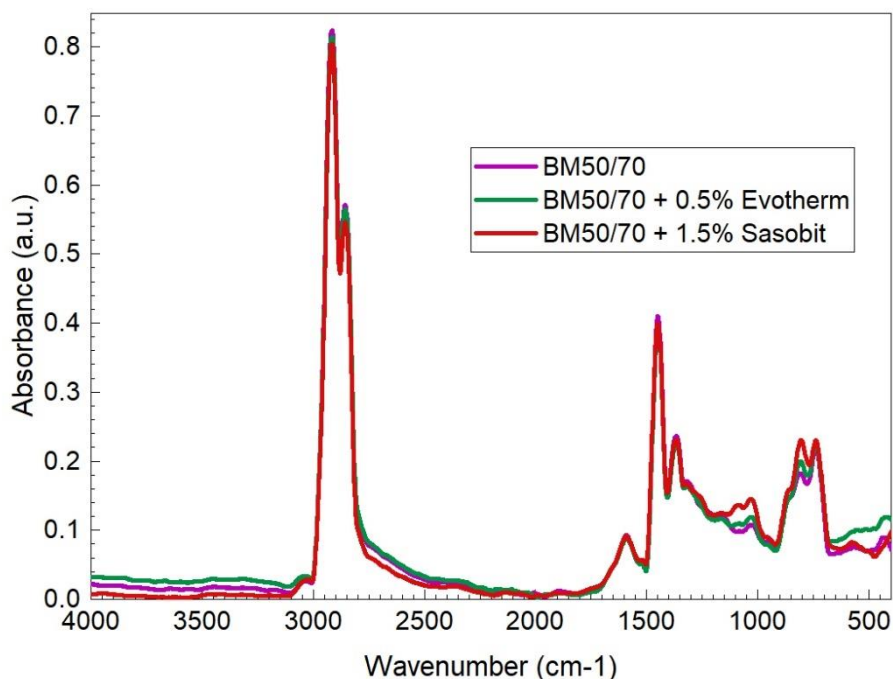


Figure 4.33. FTIR spectra of modified bituminous binder obtained from Batman refinery

Figure 4.34 displays the changes in the carbonyl and sulfoxide indexes of the KK50/70 binder, modified with Evotherm and Sasobit and exposed to aging. It's observed that adding WMA additives decreases the carbonyl index. After both short-term and long-term aging, the carbonyl index of the modified binders is lower than that of the unmodified binder. Additionally, while the Sasobit additive decreases the binder's sulfoxide index, the Evotherm additive increases the binder's sulfoxide index. Following short-term aging, the sulfoxide index value of both Sasobit and Evotherm-modified binders is higher than that of the unmodified binder. However, after long-term aging, the Evotherm-modified binder exhibits the highest sulfoxide index value, whereas the Sasobit-modified binder has the lowest sulfoxide index.

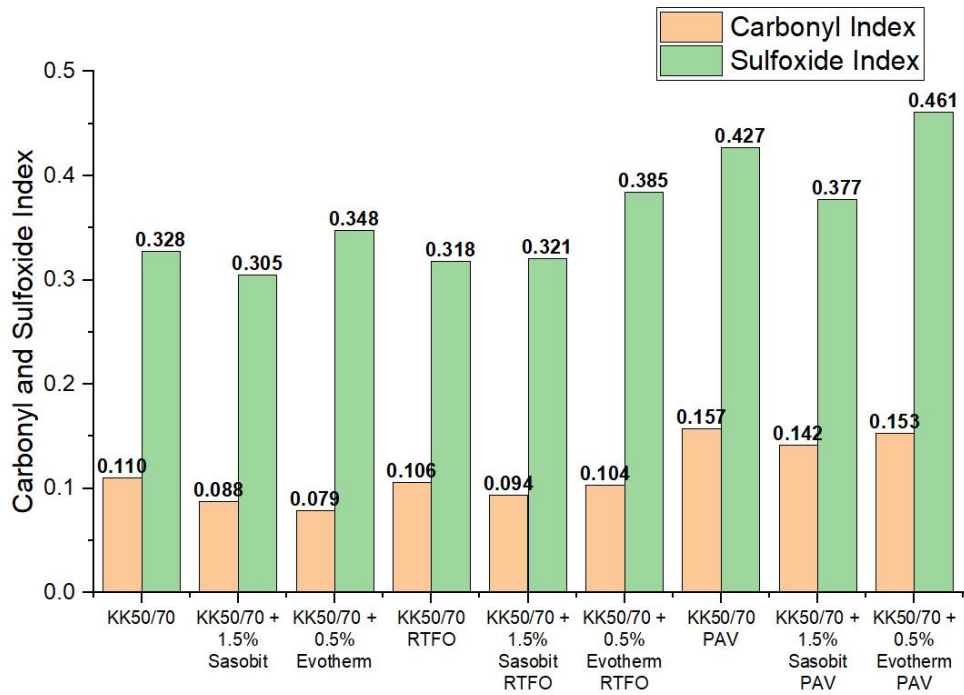


Figure 4.34. Change of the carbonyl and sulfoxide indices of modified bituminous binder (Kırıkkale Refinery)

Figure 4.35 shows the changes in the carbonyl and sulfoxide indexes of the BM50/70 binder modified with Sasobit and Evothem after short-term and long-term aging. It's observed that Sasobit and Evothem additives reduce the carbonyl index of the bituminous binder. After both short-term and long-term aging, the modified binder's carbonyl index is lower than the unmodified binder's. The binder with the lowest carbonyl index is the Evothem modified BM50/70. Similarly, it's noticed that WMA additives also reduce the binder's sulfoxide index. After both short-term and long-term aging, the sulfoxide index of the Sasobit and Evothem-modified binders is lower than that of the BM50/70 binder. While the Evothem-modified binder has the lowest sulfoxide index, the BM50/70 binder has the highest sulfoxide index.

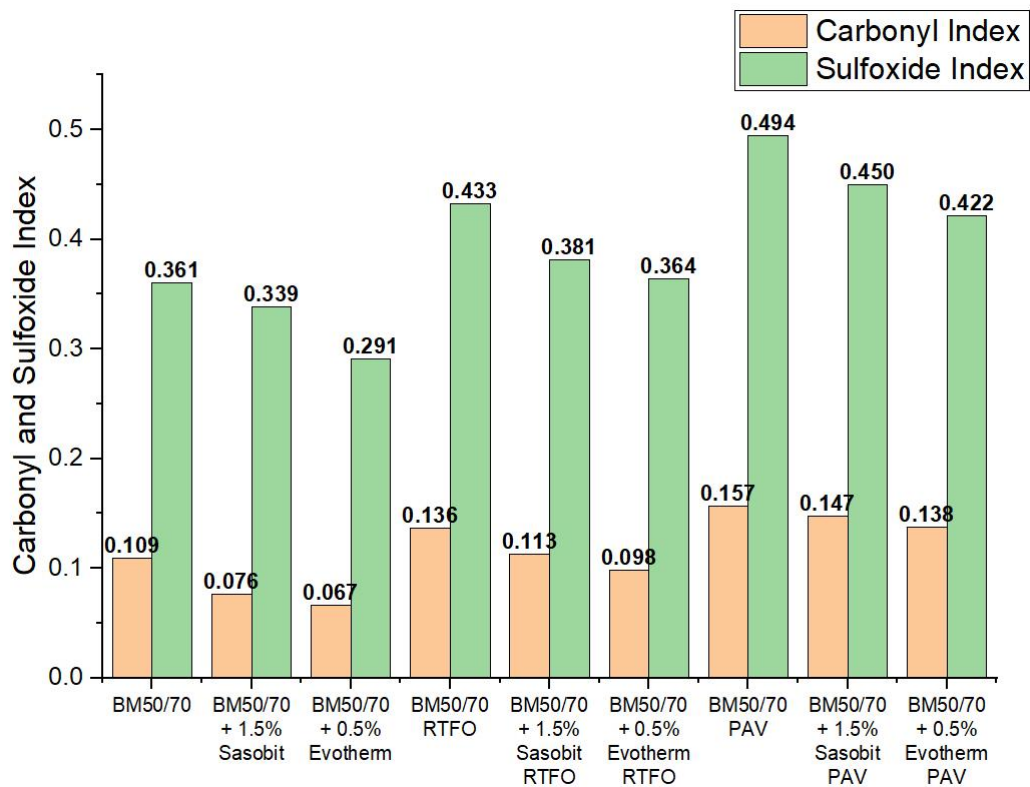


Figure 4.35. Change of the carbonyl and sulfoxide indices of modified bituminous binder (Batman Refinery)

As a result, the binder source and WMA additives influence the carbonyl and sulfoxide indexes of binders. Evotherm addition significantly reduces both the carbonyl and sulfoxide indexes of the BM50/70 binder, while for the KK50/70 binder, it only reduces the carbonyl index and increases the sulfoxide index. On the other hand, Sasobit addition reduces both the carbonyl and sulfoxide indexes of the KK50/70 and BM50/70 binders.

To further analysis these variations, the change in aging indices of modified bituminous binders obtained from the Kırıkkale refinery is presented in Figure 4.36. Evotherm additive mildly reduces the aging index of the bituminous binder, whereas Sasobit additive shows a more pronounced decrease in the binder's aging index. In the case of exposure to aging, the Sasobit additive decreases the aging index of the bituminous binder in both short-term and long-term aging. This indicates Sasobit's

assistance in reducing the impact of aging on the binder compared to the unmodified bituminous binder. However, the aging index of the Evotherm-modified binder indicates that it is significantly affected by aging than the unmodified bituminous binder. Figure 4.37 presents the change in aging indices of modified binders obtained from the Batman refinery with aging. Unlike Figure 4.36, binders obtained from the Batman refinery show a decrease in the aging index when modified with Evotherm and Sasobit additives. Following short-term and long-term aging, it is also observed that the aging index value of modified binders is lower than that of unmodified bituminous binders.

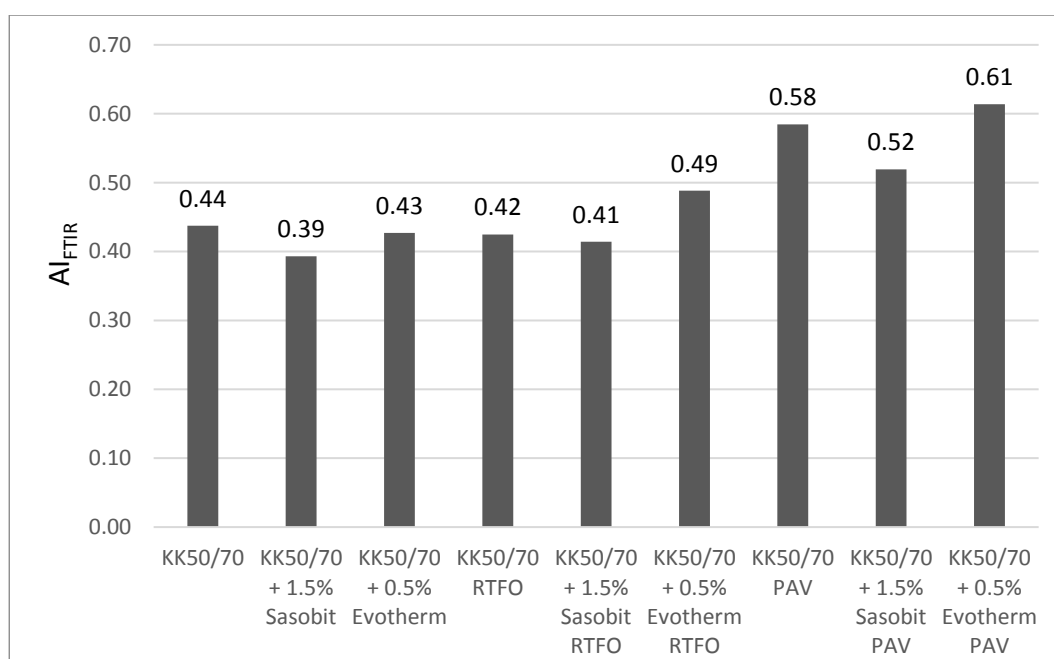


Figure 4.36. Aging indices of modified bituminous binders obtained from Kırıkkale refinery

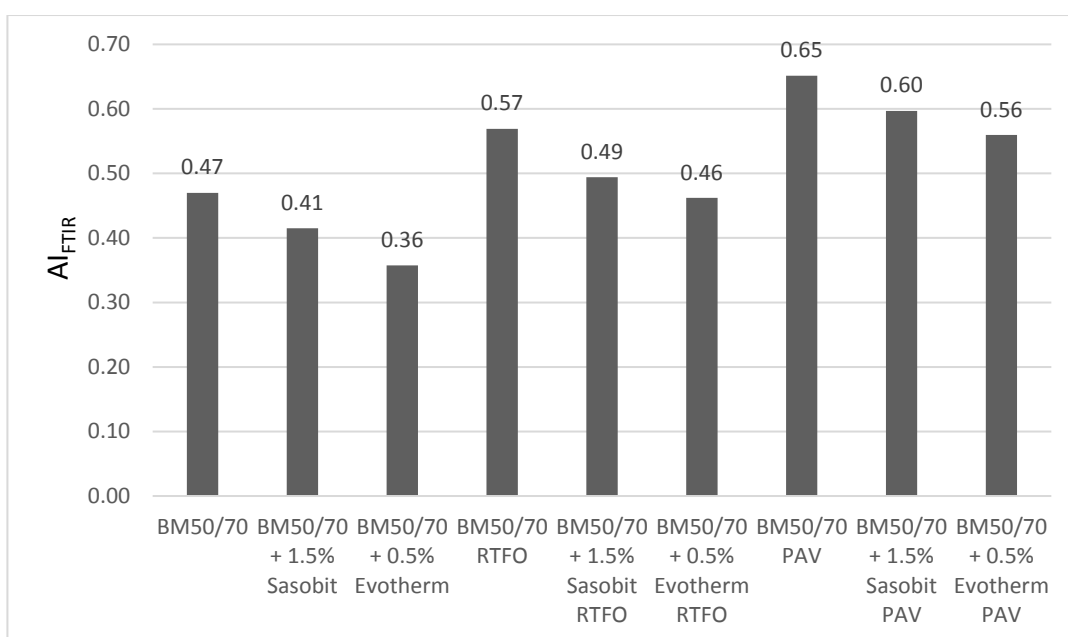


Figure 4.37. Aging indices of modified bituminous binders obtained from Batman refinery

Consequently, it is observed that the Sasobit additive consistently decreases the aging index value of binders obtained from the Kırıkkale refinery following short-term and long-term aging. On the contrary, the Evotherm additive decreases the aging index solely for BM50/70. Additionally, the Evotherm and Sasobit additives reduce the aging index of the bituminous binder obtained from the Batman refinery after undergoing short-term and long-term aging procedures. Hence, the aging index of the bituminous binder exhibits distinct responses based on both the binder source and the additive introduced into the bituminous binder.

Furthermore, in Figure 4.38, the correlation between the Gaestel and aging indices of modified bituminous binders is delineated. A positive correlation between Gaestel and aging indices in modified binders is evident, like the relationship observed in unmodified bituminous binders. The correlation between the aging and Gaestel indices have been explicitly formulated. Therefore, there is a correlation between the functional groups of bituminous binders identified through FTIR analysis and the

SARA fractions of the bituminous binder for unmodified and modified bituminous binders.

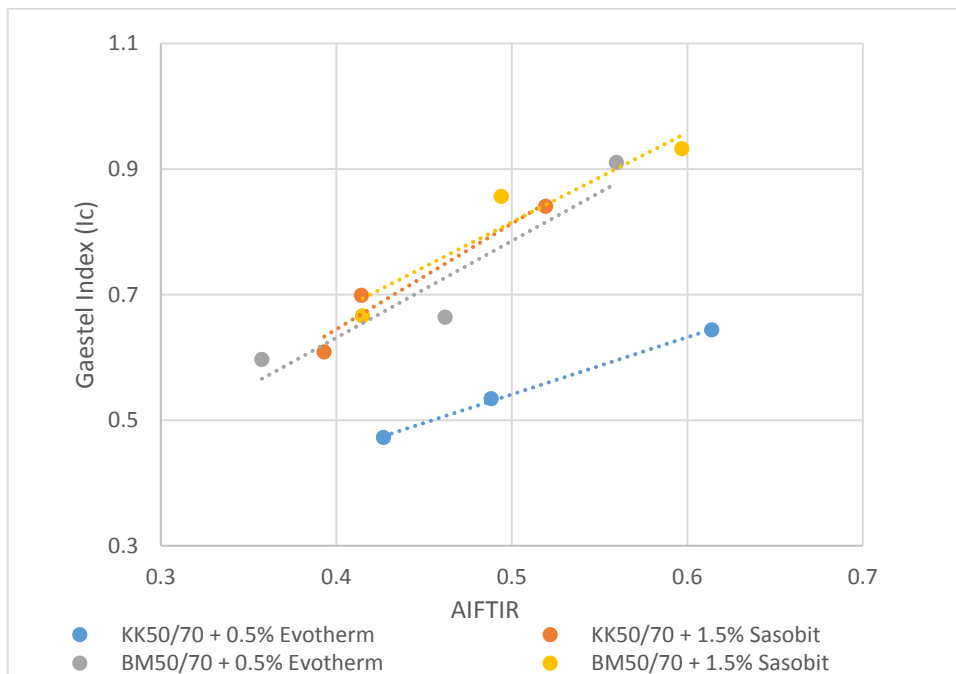


Figure 4.38. Gaestel and aging indices of modified bituminous binders

CHAPTER 5

CONCLUSION

This section summarizes the major findings obtained from the study, and recommendations for future research are also provided.

5.1 Major Findings in This Study

The outcomes of the study are presented in three subsections unmodified binders, modified binders, and common findings.

For unmodified bituminous binder:

- The bituminous binders obtained from the Batman refinery are harder in terms of physical properties compared to the bituminous binder obtained from the Kırıkkale refinery. Consequently, the viscosity of binders sourced from the Batman refinery is higher than the ones provided from Kırıkkale refinery.
- It is found out that the SARA fractions of bituminous binders obtained from different binder sources are distinct, and the difference is more pronounced among saturate and asphaltene fractions rather than the aromatic and resin fractions.
- The saturate and aromatic fractions, representing the softness of the bituminous binder, and the asphaltene and resin fractions, reflecting its hardness, correlate with the physical properties of bituminous binders. An increase in the asphaltene fraction and a decrease in the saturate fraction concurrently contribute to the hardening of the bituminous binder.

- There is a direct relationship between the asphaltene fraction and the viscosity of unmodified bituminous binder; as the asphaltene fraction increases, the viscosity of the bituminous binder increases.
- The true grades of bituminous binders obtained from the Batman refinery are higher than binders obtained from the Kırıkkale refinery for unaged and short-term aged. However, after long-term aging, the true grades of bituminous binders obtained from the Kırıkkale refinery are higher.
- The rutting resistance of binders obtained from the Batman refinery is higher than those obtained from the Kırıkkale refinery. Additionally, binders obtained from the Batman refinery had more pronounced elastic deformation behavior.
- It is observed that bituminous binders obtained from different binder sources exhibit the same trends in the alterations of SARA fractions with aging, though the variance is different.
- Aging results in change of SARA fractions of bituminous binders. An increase in the asphaltene fraction, a decrease in the aromatic fraction, and no significant change in the saturate fraction are observed. On the other hand, the resin fraction remains relatively stable after short-term aging but exhibits a notable increase following long-term aging. Also, it is revealed that the asphaltene fraction of the bituminous binder increased significantly more during long-term aging than short-term aging for bituminous binder from different binder sources.
- An increase in the asphaltene fraction leads to higher true grade, higher complex shear modulus values, decreased phase angle, and enhanced rutting resistance in the binder.
- The asphaltene fraction of bituminous binders sourced from the Batman refinery is higher than those obtained from the Kırıkkale refinery in unaged, short-term, and long-term aged conditions.
- The binders obtained from the Batman refinery are more affected by the aging process than those obtained from the Kırıkkale refinery and tend to

harden more. This is understood from the high values of the Gaestel and Aging indexes.

For WMA-modified bituminous binder:

- It is observed that although Evotherm and Sasobit are both WMA additives, Evotherm additive softens the bituminous binder without significantly affecting its viscosity. Conversely, the Sasobit additive hardens the bituminous binder while reducing its viscosity.
- Regardless of the WMA additive used, the volatile substances increase by adding the WMA additives.
- At the unaged condition, it is revealed that the Evotherm additive reduces the asphaltene and resin fractions of the bituminous binder and increases the aromatic fraction. However, the effect on the saturate fraction is noticeably different, stemming from variations in binder sources.
- At the unaged condition, the addition of Sasobit increases the asphaltene and saturate fractions of bituminous binders while reducing the resin and aromatic fractions. However, the magnitude of these effects varies depending on the source of the bituminous binder.
- The addition of Sasobit increases the asphaltene fraction while reducing viscosity, whereas the addition of Evotherm decreases asphaltene without significantly affecting viscosity. In other words, it is hard to establish a direct correlation between the asphaltene fraction and the viscosity of modified binders.
- The true grade demonstrates an increase concomitant with the increase in the asphaltene fraction. The addition of Sasobit elevates the true grade of the bituminous binder, whereas the Evotherm additive reduces the true grade of the bituminous binder.
- Sasobit additive enhances the rutting resistance of the binder and enables the binder to exhibit a more elastic deformation behavior. On the other hand, the

Evotherm additive reduces the rutting resistance of the binder and promotes a more viscous deformation behavior.

- Evotherm additive has caused a more significant alteration in the SARA composition of binders than Sasobit in the short-term aging process.
- After long-term aging, modified binders show a decrease in asphaltene and resin fractions compared to base binders. Conversely, the saturate and aromatic fractions are higher in the modified binders. The aromatic fraction of modified binders is especially significantly higher than that of unmodified binders subjected to long-term aging. This escalation signifies the increasing flexibility of the modified binders compared to the unmodified bituminous binder.
- The binders obtained and modified from the Kırıkkale refinery correlate with asphaltene ratios and true grade values. As the asphaltene ratio increases, the true grade value also increases. However, there is no discernible relationship between the asphaltene ratios and true grade values of the binders obtained and modified from the Batman refinery.
- Modified binders from Kırıkkale refinery exhibit increased rutting resistance with higher asphaltene fraction. On the other hand, binders from the Batman refinery do not demonstrate a relationship between rutting resistance and asphaltene fraction.
- The Sasobit additive increases the Gaestel index of the binder. On the other hand, the Evotherm additive either increases or decreases the Gaestel index depending on the source of the binder. While the Evotherm additive reduces the Gaestel index of binders obtained from the Kırıkkale refinery, it has slightly increased the Gaestel index of binders obtained from the Batman refinery.
- The sulfoxide indices of binders modified with Evotherm and Sasobit decrease, while the carbonyl index varies according to the source of the binder and the WMA additives.

- Sasobit and Evotherm additives reduce aging indices in binders, with a more significant decrease observed in those from the Batman refinery. Sasobit-modified binders consistently show lower aging indices than base binders after short and long-term aging. Evotherm-modified binders exhibit varying responses based on the source: in Batman refinery binders, the aging index is lower, while in Kırıkkale refinery binders, it is higher than the base binder.

For unmodified and modified binders:

- As bituminous binders are exposed to aging, there is an increase in Gaestel indices. The aging of bituminous binders is associated with increased asphaltene fractions, and thus an increase in Gaestel indices.
- The aging indices of bituminous binders experience an increase during the aging process.
- A linear relationship has been established between the Gaestel and bituminous binder aging indices.

5.2 Recommendations

According to the findings of this thesis, it arises that this study should be extended by analyzing the relationship between the low-temperature properties of WMA modified binders and SARA fractions. Additionally, this study is limited to two WMA additives with a single dosage. The effect of additive dosage has to be considered in future studies. It should be recalled that there are various WMA additives that are commonly used in the pavement industry. Moreover, in the last decade, rejuvenating agents have been used to extend or recycle the life of the pavements. The effect of these agents on the chemical, physical, and rheological properties has not been identified yet. Thus, in light of the findings of this study, the research has to be expanded in the future.

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APPENDICES

A. Rheological Data

Table A.1 The rheological parameters of bituminous binders at intermediate temperature

f=10 Hz		Temperature (°C)	
Unaged Bituminous Binder		34	40
KK50/70	G*, Pa	728600.0	290300.0
	Phase Angle (δ)	63.7	69.6
	G*/sin δ , kPa	812.8	309.6
KK70/100	G*, Pa	394000.0	155800.0
	Phase Angle, Φ	68.3	73.2
	G*/sin δ , kPa	424.2	162.7
BM50/70	G*, Pa	539400.0	279100.0
	Phase Angle (δ)	56.4	59.9
	G*/sin δ , kPa	648.0	322.7
BM70/100	G*, Pa	337400.0	172900.0
	Phase Angle (δ)	59.3	62.4
	G*/sin δ , kPa	392.4	195.1

Table A.2 Relationship between rheological parameters at high temperatures and asphaltene and maltene fractions of binders

Bituminous Binders	Asphaltene (%)	Maltene (%)	T= 58 °C, f=10 Hz			T=64°C , f=10Hz		
			G* (Pa)	Phase Angle (δ)	G*/sin δ (kPa)	G* (Pa)	Phase Angle (δ)	G*/sin δ , kPa
BM50/70 Unaged	25.0	73.3	31340.0	69.0	33.6	16150.0	72.3	17.0
BM70/100 Unaged	23.0	75.3	22990.0	71.2	24.3	12170.0	74.1	12.7

Table A.2¹ eqv_f +

KK50/70 Unaged	18.4	81.0	22020.0	79.8	22.4	10740.0	82.0	10.8
KK70/10 0 Unaged	15.5	82.1	12340.0	81.9	12.5	6148.0	83.9	6.2
BM50/70 RTFO	28.0	69.0	114200. 0	56.4	137.2	62320.0	59.5	72.3
BM70/10 0 RTFO	25.8	72.4	74810.0	59.3	87.0	40290.0	61.7	45.8
KK50/70 RTFO	23.2	76.4	83190.0	69.4	88.8	38280.0	72.8	40.1
KK70/10 0 RTFO	19.8	79.7	40350.0	74.3	41.9	18910.0	77.3	19.4
BM50/70 PAV	36.7	60.2	606700. 0	43.1	887.8	373700. 0	44.8	530.3
BM70/10 0 PAV	35.1	62.7	437000. 0	45.7	610.4	252600. 0	47.4	343.1
KK50/70 PAV	27.8	69.8	415800. 0	58.0	490.2	207700. 0	61.1	237.2
KK70/10 0 PAV	24.2	73.8	243100. 0	59.6	281.7	122500. 0	61.6	139.3

Table A.3 Asphaltene and Rheological parameters of modified KK50/70 binder at intermediate temperatures

Bituminous Binders	Asphaltene (%)	T=34°C, f=10Hz			T=40°C, f=10Hz		
		G* (Pa)	Phase Angle (δ)	G*/sinδ, kPa	G* (Pa)	Phase Angle (δ)	G*/sinδ, kPa
KK50/70 + 0.5% Evotherm	17.7	656800	65.0	725	297100	70.4	315
KK50/70	18.4	728600	63.7	812.8	290300.0	69.6	310
KK50/70 + 1.5% Sasobit	19.1	1214000	57.1	1446	571800	64.0	636
KK50/70 + 0.5% Evotherm RTFO	22.7	1344000	53.8	1666	652900	59.9	755
KK50/70 RTFO	23.4	1751000.0	49.4	2305	895800	55.9	1082
KK50/70 + 1.5% Sasobit RTFO	23.5	2092000	45.5	2933	1074000	53.0	1344
KK50/70 + 0.5% Evotherm PAV	25.1	5599000	44.4	8000	2669000	49.3	3518
KK50/70 PAV	27.8	7277000.0	42.0	10873	3585000	46.4	4948
KK50/70 + 1.5% Sasobit PAV	28.6	7543000	40.2	10874	3835000	43.7	4949

Table A.4 Asphaltene and Rheological parameters of modified BM50/70 binder at intermediate temperatures

Bituminous Binders	Asphaltene (%)	T=34°C, f=10Hz			T=40°C, f=10Hz		
		G* (Pa)	Phase Angle (δ)	G*/sin δ , kPa	G* (Pa)	Phase Angle (δ)	G*/sin δ , kPa
BM50/70 + 0.5% Evotherm	24.4	553800	56.1	668	282700	59.6	328
BM50/70	25	539400	56.4	648	279100.0	59.9	323
BM50/70 + 1.5% Sasobit	26.1	847700	49.8	1110	446000	54.9	545
BM50/70 RTFO	28.0	1454000	43.3	2119	806500	47.3	1098
BM50/70 + 0.5% Evotherm RTFO	29.0	1456000	44.2	2088	798700	48.2	1072
BM50/70 + 1.5% Sasobit RTFO	29.3	2074000	38.2	3352	1163000	43.5	1689
BM50/70 + 1.5% Sasobit PAV	33.6	6970000	34.3	12378	3910000	36.8	6530
BM50/70 + 0.5% Evotherm PAV	33.8	6738000	40.0	2120	3532000	43.7	1099
BM50/70 PAV	36.7	5193000	35.1	9022	2846000	37.5	4672

B. FTIR Graphs

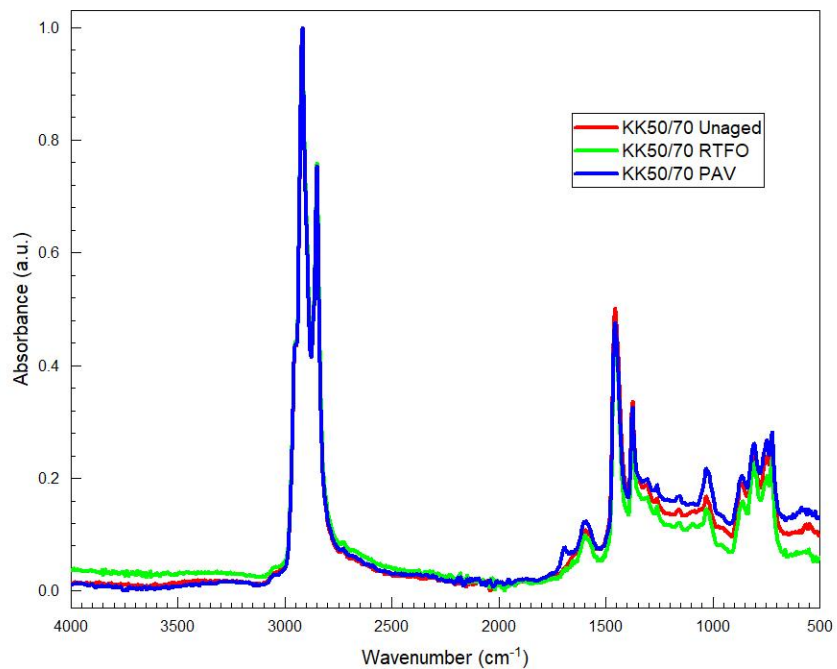


Figure B.1 FTIR spectra of KK50/70 with aging

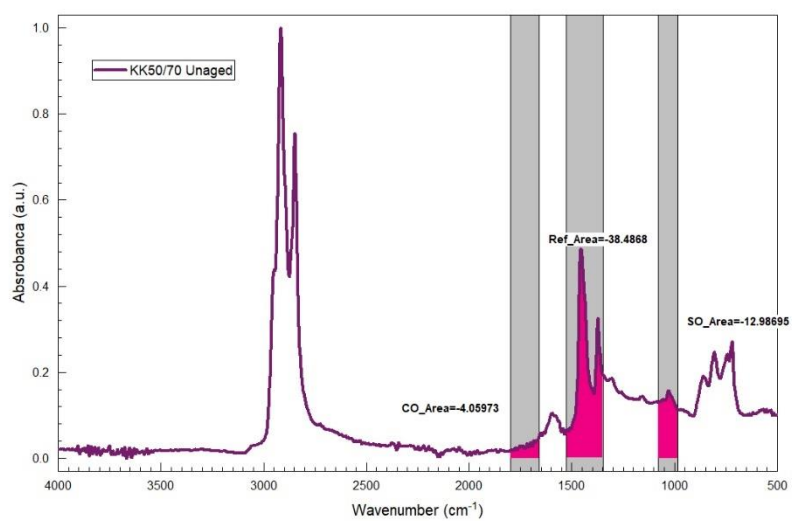


Figure B.2 Integrated CO, SO and Ref Areas of KK50/70 Unaged spectra

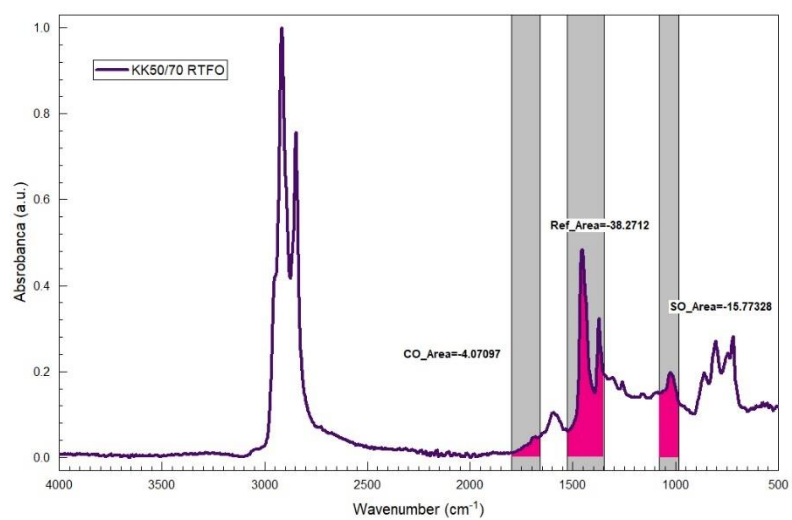


Figure B.3 Integrated CO, SO and Ref Areas of KK50/70 RTFO spectra

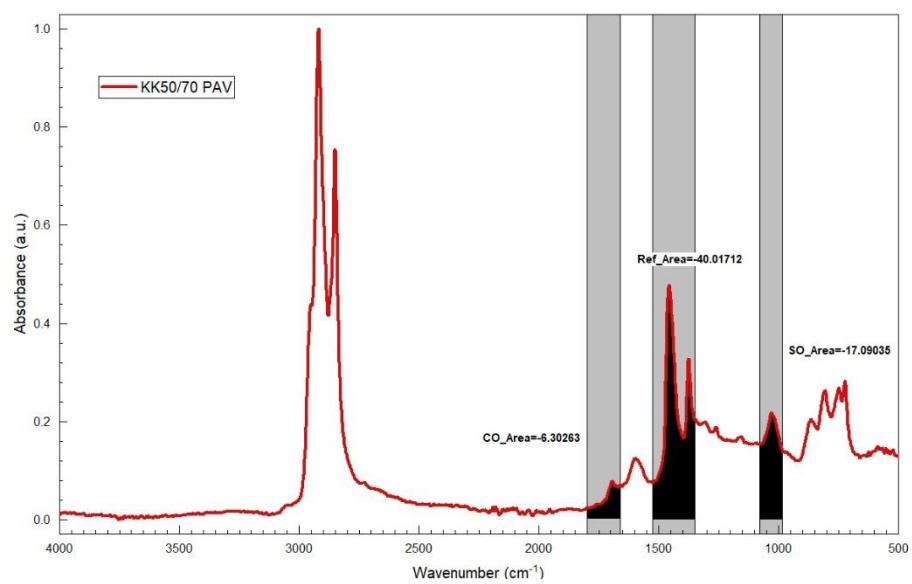


Figure B.4 Integrated CO, SO and Ref Areas of KK50/70 PAV spectra

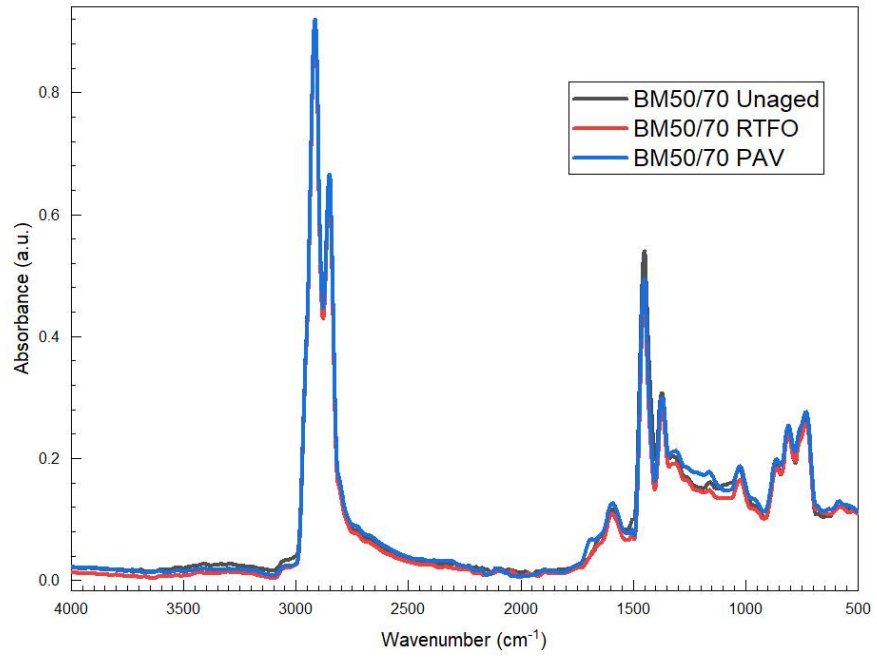


Figure B.5 FTIR spectra of BM50/70 with aging

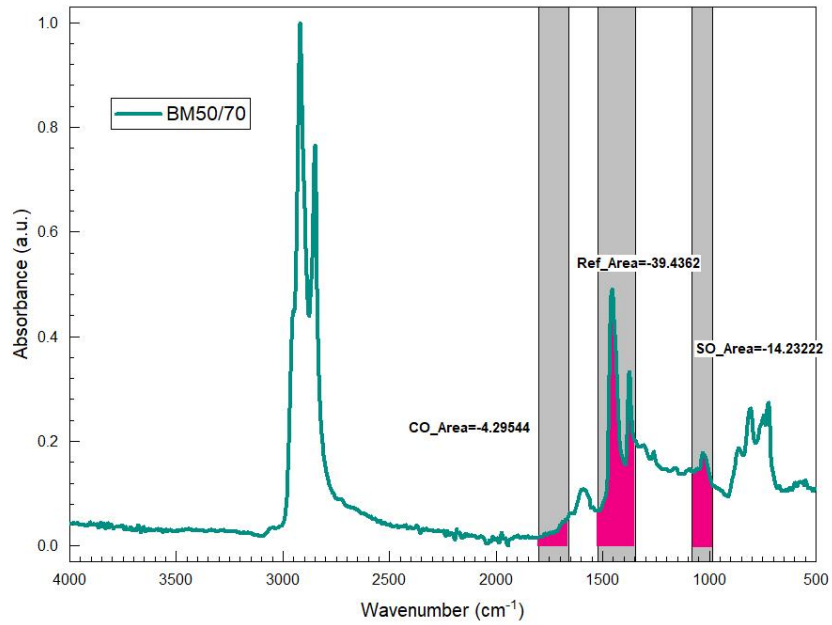


Figure B.6 Figure B.4 Integrated CO, SO and Ref Areas of BM50/70 Unaged spectra

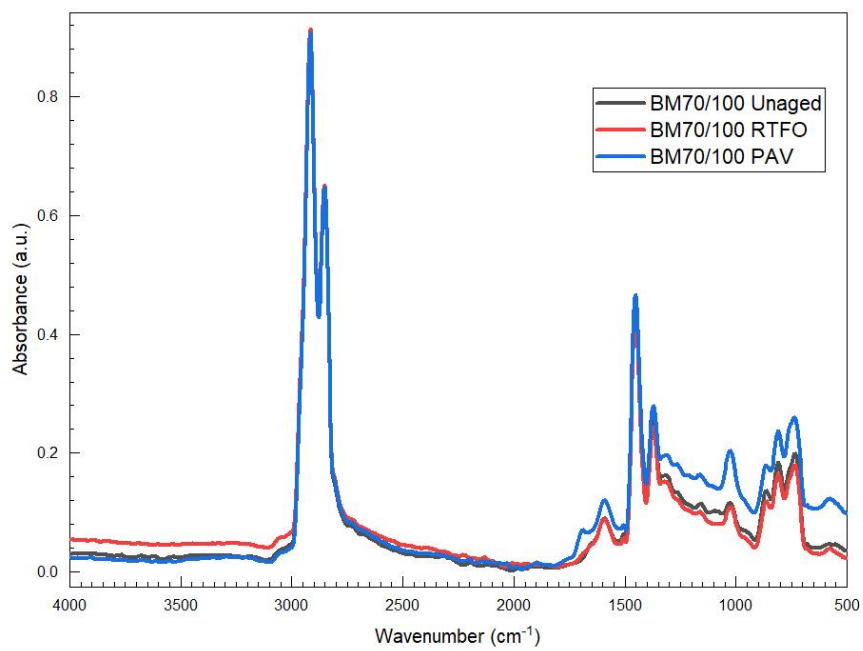


Figure B.7 FTIR spectra of BM70/100 with aging

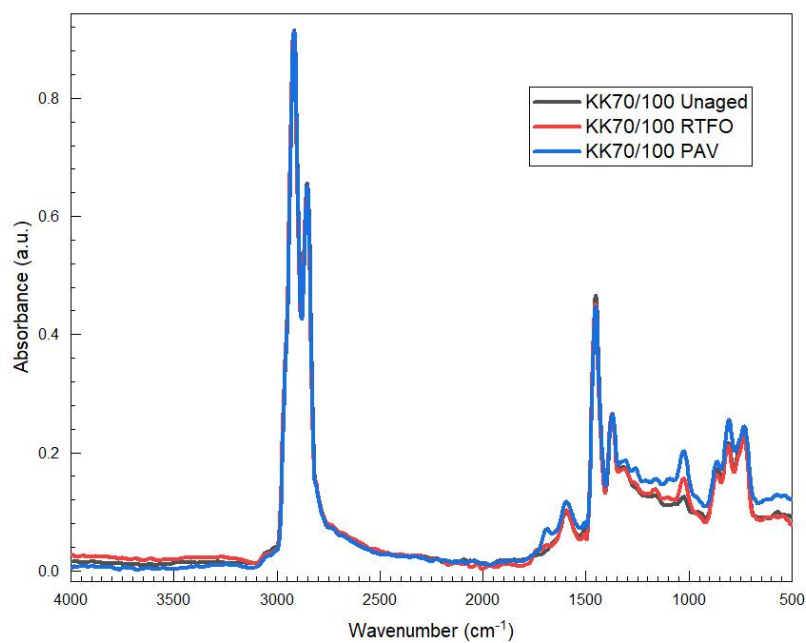


Figure B.8 FTIR spectra of KK70/100 with aging

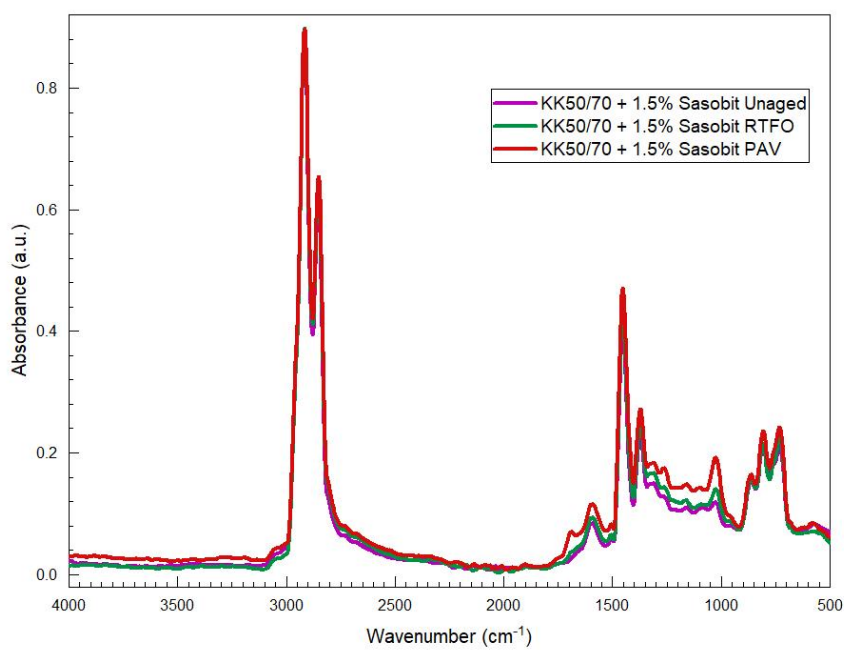


Figure B.9. FTIR spectra of KK50/70 + 1.5% Sasobit with aging

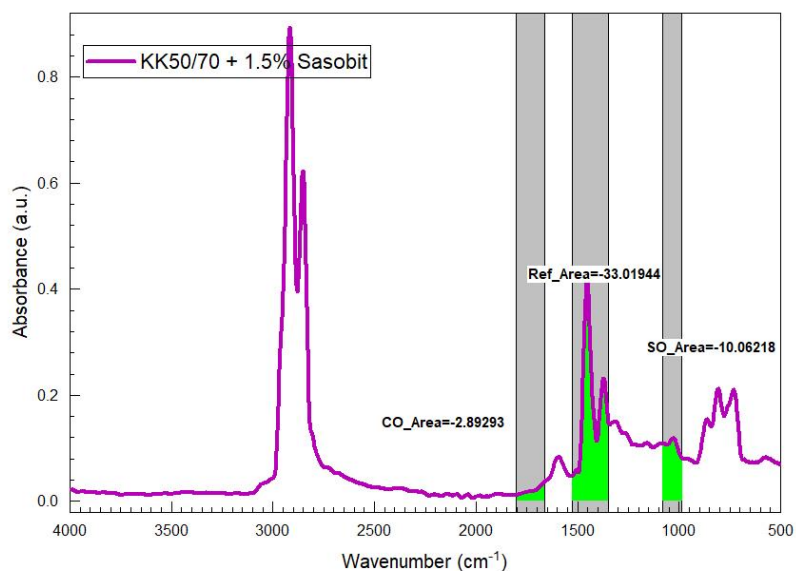


Figure B.10 Integrated CO, SO and Ref Areas of KK50/70 + 1.5% Sasobit Unaged spectra

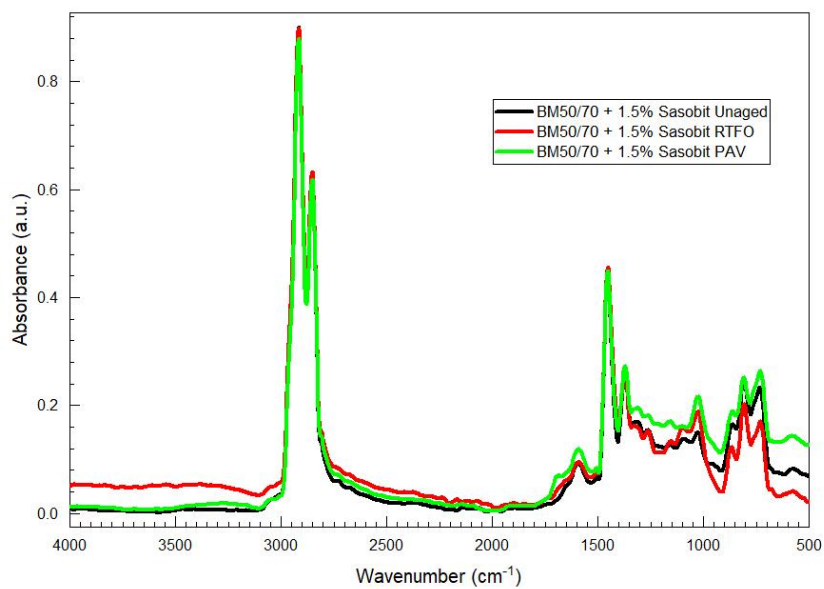


Figure B.11 FTIR spectra of BM50/70 + 1.5% Sasobit with aging

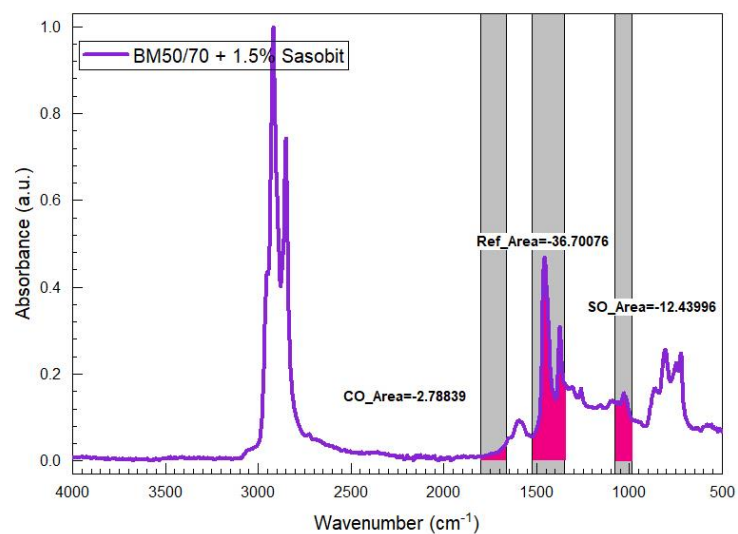


Figure B.12 Integrated CO, SO and Ref Areas of BM50/70 + 1.5% Sasobit Unaged spectra

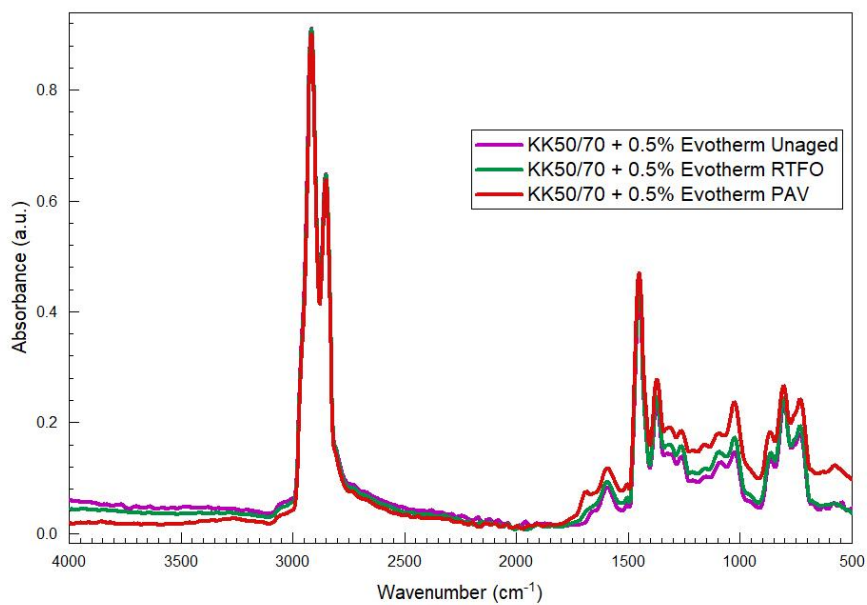


Figure B.13 FTIR spectra of KK50/70 + 0.5% Evotherm with aging

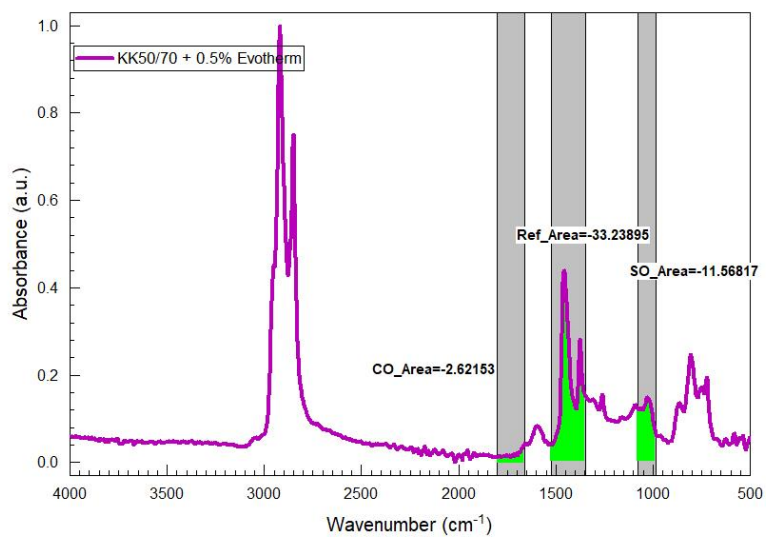


Figure B.14 Integrated CO, SO and Ref Areas of KK50/70 + 0.5% Evotherm
Unaged spectra

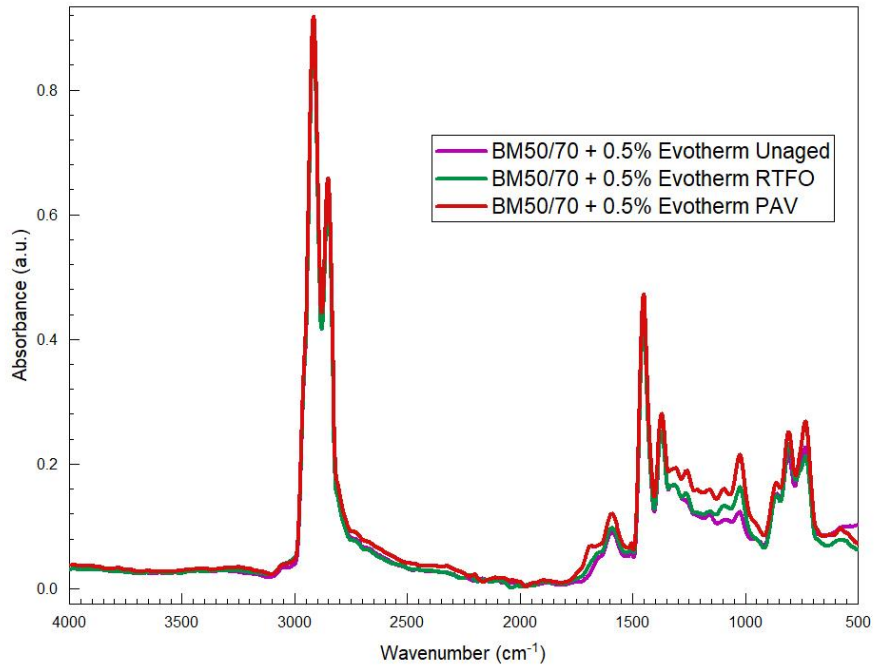


Figure B.15 FTIR spectra of BM50/70 + 0.5% Evotharm with aging

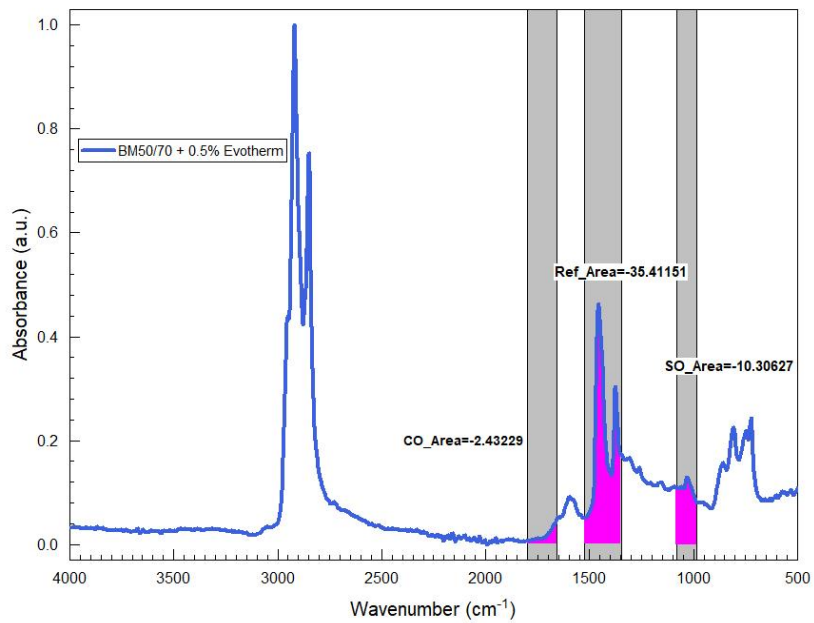


Figure B.15 Integrated CO, SO and Ref Areas of BM50/70 + 0.5% Evotharm Unaged spectra