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Evaluation of Saturates/Aromatics/Resins/Asphaltenes (SARA) Fractionation of Asphalt Binders in Louisiana

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13. Abstract
State and federal agencies face ongoing challenges in the characterization and qualification of diverse paving materials. Although conventional asphalt binder characterization relies on extensive rheological and mixture testing, these methods often leave long-term performance characterization uncertain. Consequently, agencies are exploring faster, more precise chemical testing at the molecular level.

Gel Permeation Chromatography (GPC) is a standard tool for binder characterization. However, its high operational and maintenance costs, combined with its limited ability to provide detailed chemical insights, have prompted interest in alternative methods. SARA (saturates, aromatics, resins, and asphaltenes) fractionation using Thin-Layer Chromatography/Flame Ionization Detection (TLC/FID) equipment offers a more efficient alternative. This study evaluated the GPC method alongside two SARA approaches: the 4-peak method, which analyzes the whole

sample directly, and the 3-peak method, which precipitates and separates asphaltenes first before grouping the remaining fractions. An analysis of 46 asphalt binder samples revealed significant differences between GPC and SARA results, with limited correlation between the methods. Additionally, an ANOVA comparison of the 3-peak and 4-peak methods showed significant differences in 55% of the samples. Based on these findings, GPC remains the superior tool for analyzing larger molecular weight distributions and polymer content detection, while SARA grouping is recommended for evaluating smaller molecular components and chemical fractions. Although both SARA methods showed similar performance, the 3-peak method showed better correlation to GPC data, while the 4-peak method was more practical.

Analysis of the chemical components across various suppliers revealed uniform colloidal stability. This indicates that formulation strategies for all binders, including polymer-modified varieties, successfully balanced the solvent phases (i.e., aromatics and resins). This balance ensures effective asphaltene peptization, despite SARA results showing distinct chemical "fingerprints" between different suppliers.

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Evaluation of Saturates/Aromatics/Resins/Asphaltenes (SARA) Fractionation of Asphalt Binders in Louisiana

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Acknowledgements

The authors acknowledge the financial support for this study by the Federal Highway Administration (FHWA), Louisiana Department of Transportation and Development (DOTD), and Louisiana Transportation Research Center (LTRC). The efforts of Jeremy Icenogle, Hannah Boggs and Angela LeMay at LTRC Asphalt Laboratory are highly appreciated.

Implementation Statement

This study established optimized procedures for the efficient characterization of asphalt binders. Although multiple analytical techniques are available, the study demonstrates that Gel Permeation Chromatography (GPC) can be effectively implemented to analyze the asphaltene and polymer components of asphalt binders based on molecular size. Conversely, SARA fractionation is identified as the more suitable method for evaluating maltene components. Given that the various SARA fractionation methods utilizing the Iatroscan yielded comparable results in most cases, the 4-peak method is recommended as the most practical and efficient approach for future implementation due to its relative simplicity.

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Introduction

For several years, the Louisiana Department of Transportation and Development (DOTD) has employed various characterization methods to evaluate asphalt binder parameters. While these efforts have primarily concentrated on physical and rheological properties, comprehensive chemical characterization has historically been less emphasized. Although DOTD currently utilizes Gel Permeation Chromatography (GPC) for chemical analysis, numerous studies [1] [2] have shown that a binder's broader chemical composition is a critical determinant of performance. These chemical properties directly affect aging, cracking resistance, and thermal stress. Therefore, there is a critical need to further evaluate the chemical components of asphalt binders to define their fundamental relationship with physical performance.

Conventional asphalt binders typically consist of five categories of hydrocarbon molecules: saturates, aromatics, resins, asphaltenes, and polymers. To identify these components, Louisiana utilizes Gel Permeation Chromatography (GPC), a technique that characterizes binder samples by separating their molecular components based on size. While GPC has significantly advanced the field of binder characterization, the method relies on the assumption that molecular size directly correlates with and accurately represents the specific chemical categories of the asphalt molecules. Although chemical properties vary across molecule types, each category typically spans a range of molecular sizes. While medium to large molecular weight components are generally assumed to be asphaltenes and polymers, this assumption is often inaccurate because maltene fractions (i.e., saturates, aromatics, and resins) can also contain large molecules. A more accurate way to distinguish these particles from one another is to use their chemical properties in the form of solubility in different solvents. This method, called SARA (saturates, aromatics, resins, and asphaltenes) fractionation, separates the binder fractions by using hexane and toluene as solvents. Different categories of molecules can be filtered and separated from one another by their solubility or insolubility in these solvents. The collecting filters are then weighed to determine the percentage of each component in the asphalt binder.

Once the chemical analysis is complete, the chemical properties can be correlated with the physical and mechanical properties of asphalt binders and mixtures. This approach facilitates the selection of higher-quality binders for roadway applications. However, conventional SARA fractionation has notable drawbacks: it requires significant quantities of solvents for very small binder samples and necessitates a complex, closed system of specialized

containers and connections. Further, the process is highly time-consuming, making it less practical for high-throughput laboratory environments that must analyze multiple samples daily.

To address these limitations, Thin-Layer Chromatography coupled with Flame-Ionization Detection (TLC-FID) provides a micro-scale alternative to conventional SARA fractionation. This method utilizes capillary action to significantly reduce both solvent consumption and analysis time. In this approach, quartz rods (i.e., Chromarods) coated with an asphalt solution are partially submerged in a sequence of solvent development tanks. As the solvents migrate up the rods via capillary action, they separate the binder into its constituent fractions. The rods are then passed through a hydrogen flame, which combusts the components; a sensor records the resulting flame intensity, which is directly proportional to the concentration of each specific binder fraction.

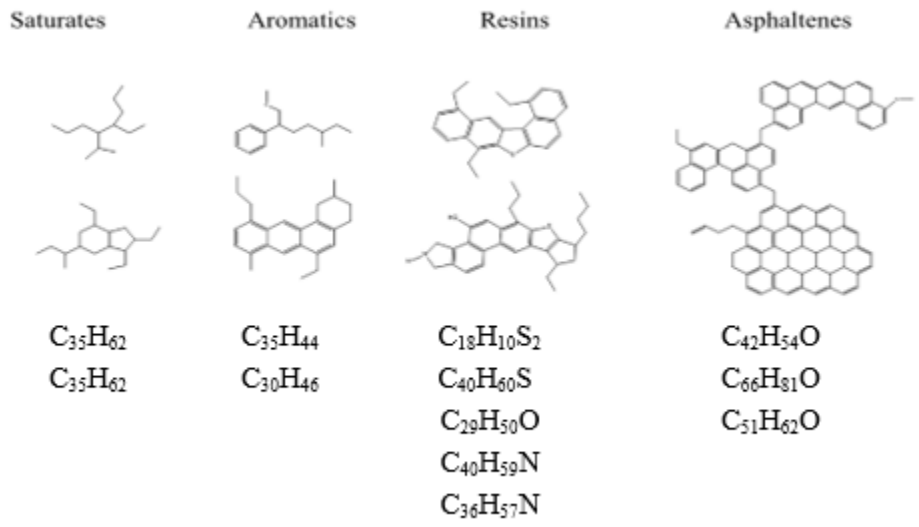
Given the significant impact of chemical composition on asphalt binder performance, a thorough comparison of these characterization methods is essential. Such an analysis is necessary to develop a comprehensive understanding of their distinct capabilities and the relative differences in their results.

Background

A major contributor to the performance of asphalt pavements is the quality of the asphalt binder in the mixture [1]. The chemical properties of asphalt binder play a critical role in determining its performance. As a byproduct of the oil refining process, the characteristics of asphalt binder are influenced by the specific chemical compounds and additives used during refining.

A widely accepted method for categorizing the complex molecular structure of asphalt binder is by dividing it into four groups: saturates, aromatics, resins, and asphaltenes, collectively known as the SARA fractions [2]. Saturates consist primarily of n-alkanes with minimal aromatic content, while aromatics contain aromatic rings and some heteroatoms. Resins and asphaltenes are more polar; however, resins have a lower molecular mass. Asphaltenes, the heaviest fraction, are composed of condensed aromatic rings and heteroatoms such as nitrogen, sulfur, and metals. Within the binder, asphaltenes and resins act as dispersed phases in a continuous matrix of saturates and aromatics [2].

Figure 1**. SARA group composition [3]**



A traditional method for separating these fractions relies on differences in solubility and polarity. ASTM D4127 outlines this SARA-based approach, which, while effective, is costly and labor-intensive. Handle et al. [4] introduced an alternative method, Thin-Layer Chromatography with Flame-Ionization Detection (TLC-FID), to improve accuracy and

reduce solvent usage. Although this method is faster and more efficient, a limitation is that the separated fractions cannot be collected for further analysis.

On a broader scale, saturates, aromatics, and resins make up the n-alkane-soluble components of asphalt, known as maltenes. Cooper et al. [5] reported that maltenes have an average molecular weight of 700 to 900 Daltons, whereas asphaltenes range between 2,000 and 10,000 Daltons. This molecular model has been used to study the correlation between the chemical composition of asphalt binders and their long-term physical performance. The model is used in conjunction with Gel Permeation Chromatography (GPC).

To enhance the precision of SARA fractionation, advanced instrumentation has been developed that integrates Thin-Layer Chromatography (TLC) and Flame Ionization Detection (FID) technologies [6].

Objective

The objective of this study was to evaluate asphalt binder characterization utilizing SARA fractionation performed via Thin-Layer Chromatography with Flame Ionization Detection (TLC/FID). These results were analyzed alongside available Gel Permeation Chromatography (GPC) data. A primary focus of this study was to investigate the sensitivity and capability of the TLC/FID-based SARA method in detecting variations in the chemical composition of asphalt binders. Further, these chemical profiles were correlated with established performance data to assess the feasibility of using TLC/FID results to predict early-age binder behavior and long-term pavement performance.

Scope

To ensure a comprehensive evaluation, this study involved the collection of asphalt binders from various terminal and plant-blend suppliers. SARA fractionation via TLC/FID was performed on these samples to establish a detailed chemical profile of the binders currently utilized throughout Louisiana. These results were compared with historical and concurrent DOTD characterization data to evaluate the effectiveness of the methodology in detecting binder modifications. Ultimately, this comparative analysis enhanced testing proficiency and supported DOTD's efforts to ensure the reliability and quality of materials utilized in state paving projects.

Methodology

Experimental Plan

A total of 46 asphalt binder samples were collected from various suppliers across Louisiana. Table 1 summarizes the sample quantities and their respective Performance Grades (PG) by producer. These binders, representing a range of collection intervals and PG classifications, were evaluated using each characterization method to compare their relative efficacy in identifying molecular components.

Table 1. List of asphalt binder samples

Sample source	Number of samples	Performance Grade of the samples
Supplier 1	4	67-22
	2	70-22M
	3	76-22M
Supplier 2	3	67-22
	3	70-22
	3	76-22
Supplier 3	3	67-22
	2	76-22M
Supplier 4	3	67-22
Supplier 5	1	70-22
	1	67-22E
	1	67-22H
	2	67-22H
	4	67-22
Supplier 6	2	58-28
	3	67-22
	3	70-22
	3	76-22

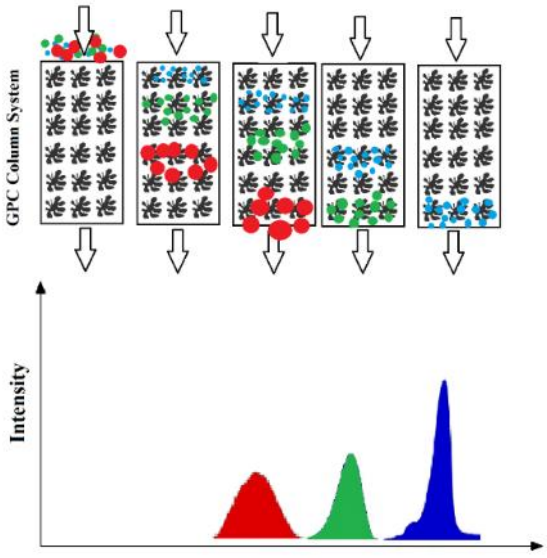
Gel Permeation Chromatography

Louisiana DOTD has adopted Gel Permeation Chromatography (GPC), which is also known as size exclusion chromatography, as a primary analytical tool for characterizing the molecular components of asphalt binders. During this procedure, a binder sample is dissolved in Tetrahydrofuran (THF) to create a dilute solution. This solution is injected into the GPC

system and transported by a mobile phase through a set of chromatography columns. These columns are packed with a porous, crosslinked polymer network that separates molecules based on their size and shape in the solution.

The separation mechanism within the column depends on the hydrodynamic volume of the molecules relative to the pores in the column packing. Molecules that are larger than the pores are totally excluded from entering the pores and therefore exit first. In contrast, very small molecules can remain stationary in the pores, which causes them to be retained longer and appear last in the results. Intermediate-sized molecules elute at different times depending on their relative sizes. As the size-separated molecules emerge from the columns, a Differential Refractive Index (DRI) detector measures their concentration. This data is used to generate a chromatogram that relates elution time to specific components, such as polymers, asphaltenes, and maltenes. Figure 2 conceptually illustrates the GPC separation process and the resulting chromogram.

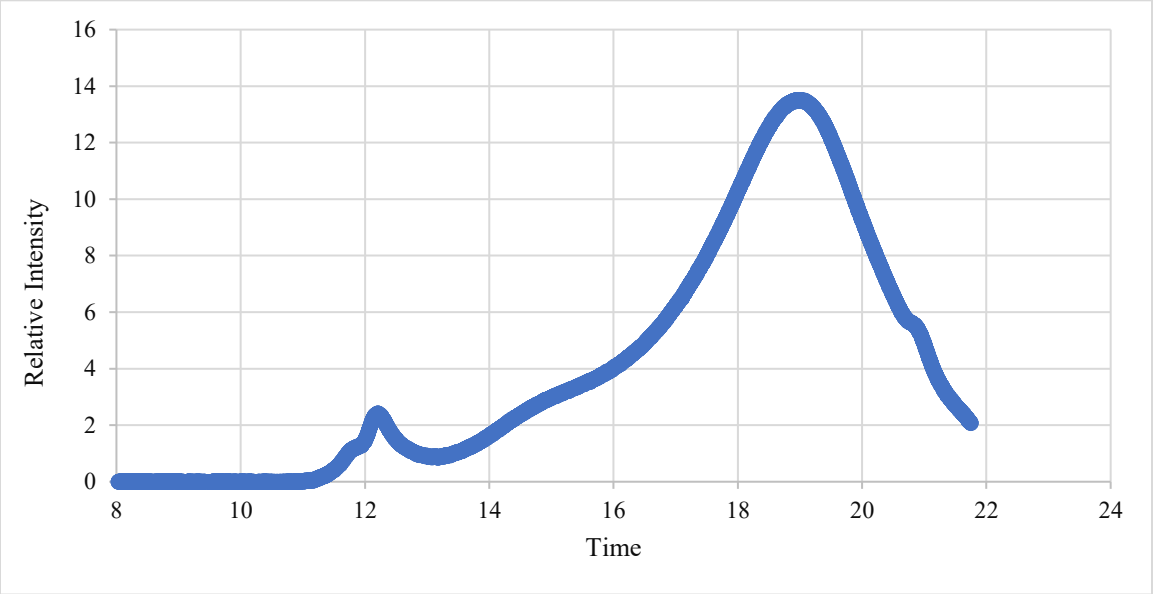
Figure 2. GPC method



GPC device

Based on the GPC method, graphs of material intensity versus molecular weight can be generated for asphalt binders; see Figure 3. In this figure, the first peak corresponds to larger polymers, which eluted from the GPC columns earlier. The second and third peaks represented asphaltenes and maltenes, respectively. Although the components of asphalt binder (i.e., asphaltenes, maltenes, and polymers) exhibit a wide range of molecular weights, previous research has established molecular weight boundaries that allow the quantification of each component [5]. These boundaries defined polymers as species with molecular weights greater than 19,000 Daltons, asphaltenes between 19,000 and 3,000 Daltons, and maltenes below 3,000 Daltons.

Figure 3. Sup6-76N202 GPC results

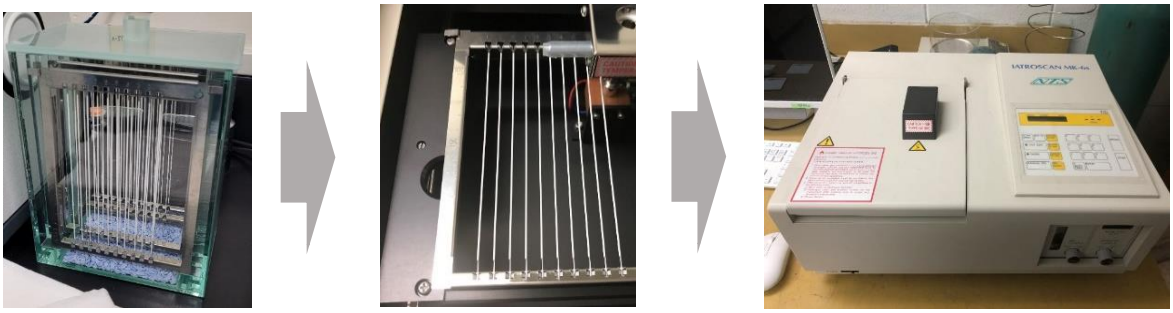


SARA Fractionation

SARA fractionation was established as a standard test method to determine the specific molecular categories within an asphalt binder. The historical approach utilizes different sections and various solvents to isolate components based on their selective solubility. This method categorizes the asphalt binder components based on their chemical nature and solubility rather than relying on an assumption of their molecular sizes, as is the case with GPC. However, the conventional process requires considerable time and large quantities of solvent, which makes it difficult to implement for routine laboratory testing. Recently, equipment was developed to adopt the SARA fractionation method using a much smaller volume of solvent within a faster timeframe. This equipment utilizes the Thin-Layer

Chromatography and Flame Ionization Detection (TLC/FID) method. In this procedure, a very small amount of sample solution is placed on highly absorbent quartz rods. The rods are placed vertically in containers with different solvent combinations, such as n-heptane, n-hexane, toluene, and methanol. Each solvent belongs to a specific molecular category and moves up the rod by capillary action. The rods are then placed in an oven to evaporate the solvents. Finally, a flame is passed over the horizontal rods, and sensors are activated to record the hydrocarbon exhaust to determine the concentrations of the separated fractions. The procedure is illustrated in Figure 4.

Figure 4. SARA grouping through TLC/FID



SARA fractionation was conducted using the TLC/FID equipment through two distinct approaches. The 3-peak method, shown in Figure 5, involved filtering out the asphaltene fraction before analysis. This allowed the limited length of the rod to be used entirely for the three maltene components (i.e., saturates, aromatics, and resins). The resulting chromatogram displayed three peaks, with each representing one of these maltene components. In contrast, the 4-peak method, shown in Figure 6, did not involve filtering out the asphaltenes. In this approach, the TLC/FID equipment output displayed four distinct peaks, representing each SARA fraction, including the asphaltene.

Figure 5. SARA (3-peak) for Sup6-76N202 results

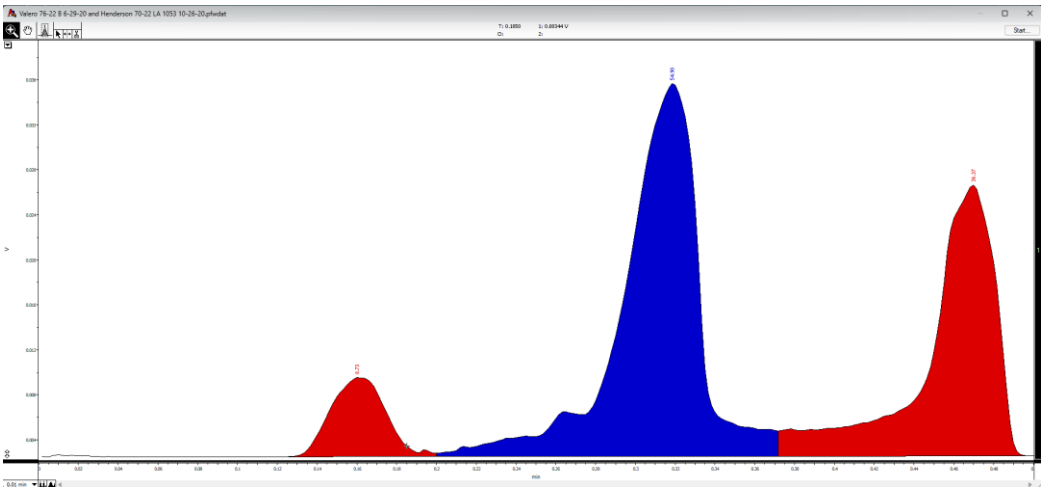
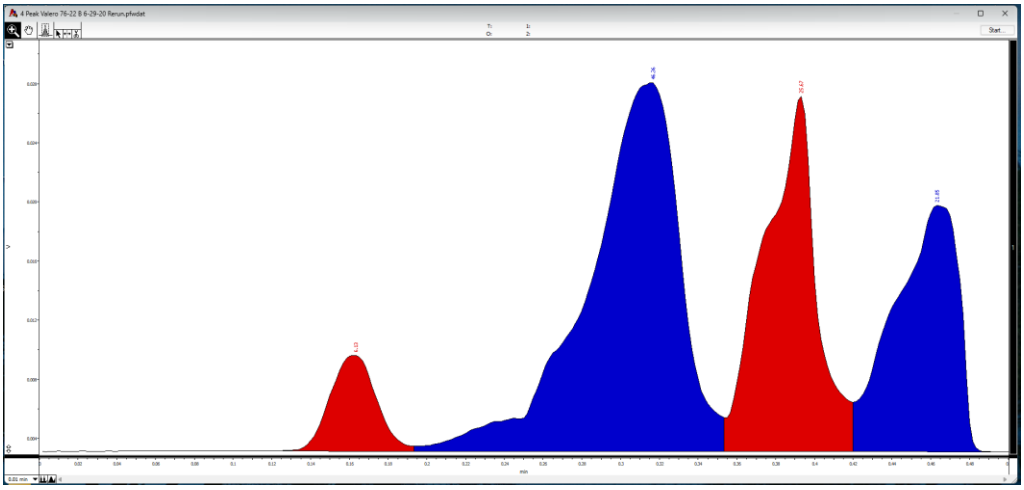


Figure 6. SARA (4-peak) for Sup6-76N202



Discussion of Results

To evaluate various test methods for characterizing the molecular components of asphalt binder, 46 modified binders were collected from local suppliers across Louisiana. These samples were analyzed to determine their specific asphaltene, polymer, and maltene contents.

GPC Test Results

Gel Permeation Chromatography (GPC) was performed on all samples to separate the components of the asphalt binder based on molecular weight. This methodology categorized the components into three distinct groups: polymers, asphaltenes, and maltenes.

SARA Test Results

SARA fractionation was conducted via TLC/FID using two distinct approaches. In the first approach, asphaltene components were screened out to allow the limited rod length to be used exclusively for the three maltene components (i.e., saturates, aromatics, and resins). Consequently, the resulting graph consisted of three peaks, one for each component. This approach was designated as the 3-peak method. The second approach, the 4-peak method, did not remove asphaltenes and produced a graph with four distinct peaks.

Because the specific components analyzed by SARA fractionation and GPC differ, adjustments were made to ensure that the datasets were comparable. For the SARA fractionation, saturates, aromatics, and resins were combined into the maltene fraction. For GPC, the asphaltene and polymer fractions were combined into a single, broader asphaltene group. Based on this adjustment, the asphalt binder was considered to consist solely of the asphaltene or maltenes group. This classification enabled GPC and SARA results to be shown with a common representative component (asphaltene) structure for the test method; see Figure 7.

Figure 7a. Asphaltene content percentage of PG 67-22 based on test method

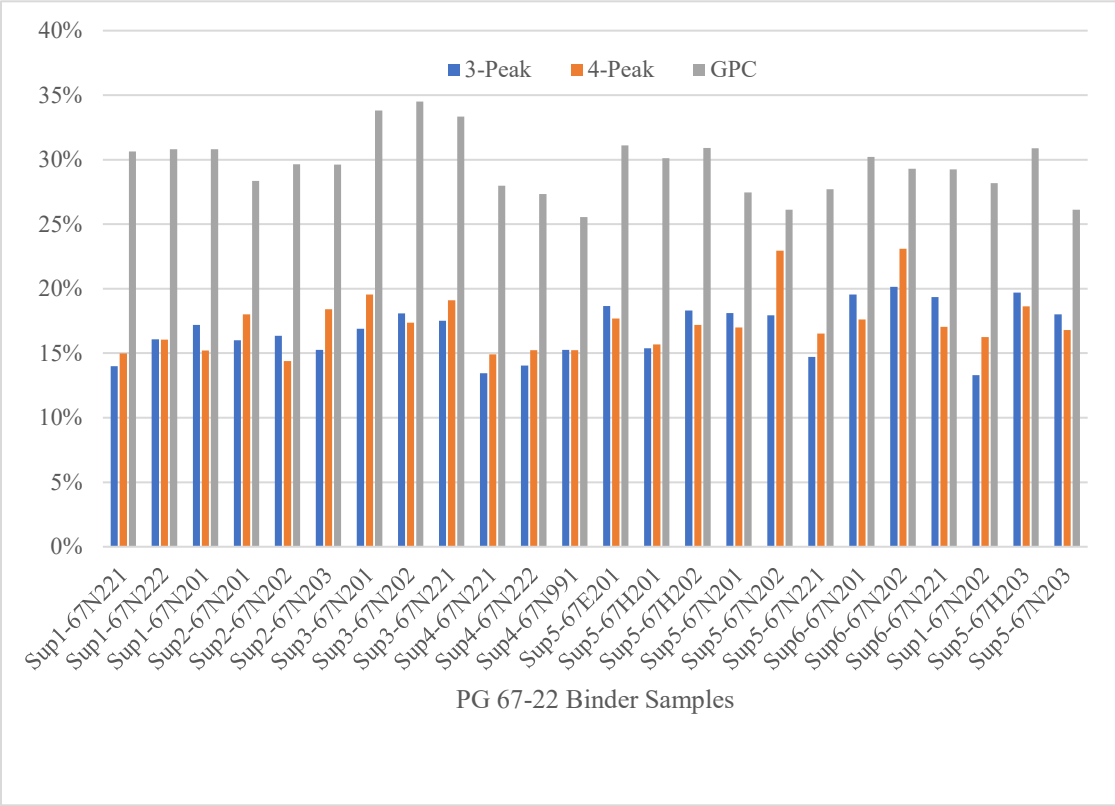


Figure 7b. Asphaltene content percentage of PG 58-28, 70-22, and 76-22 based on test method

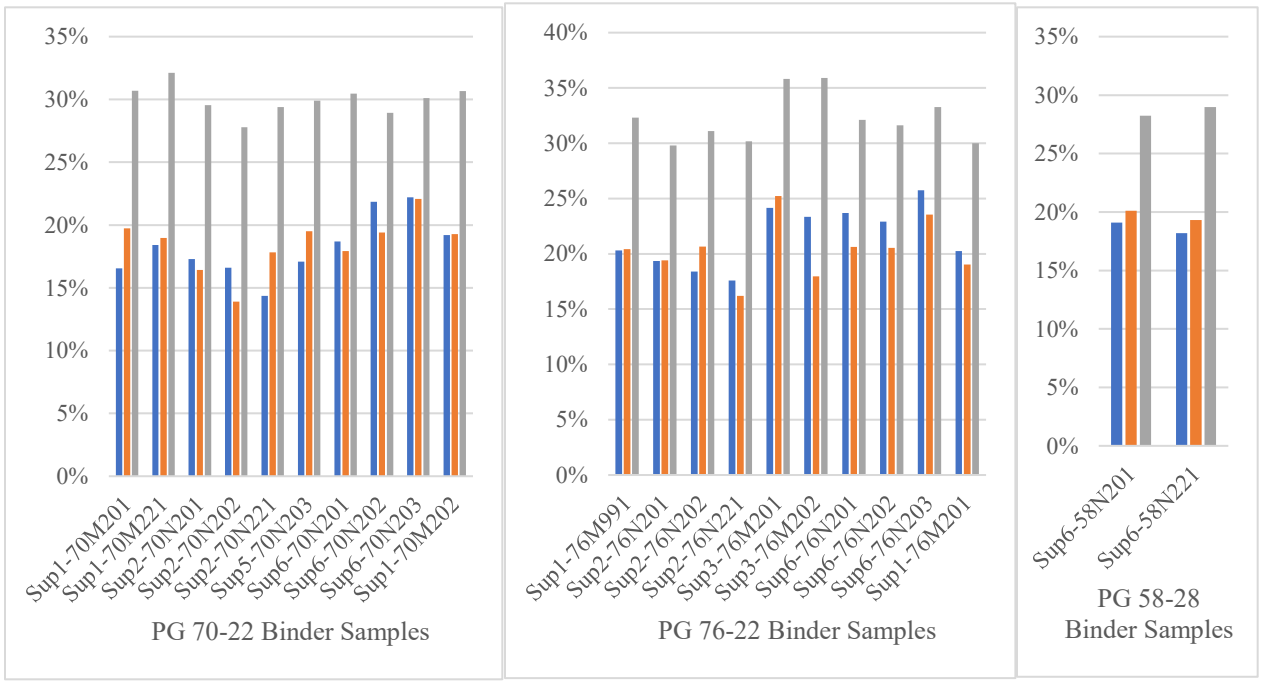


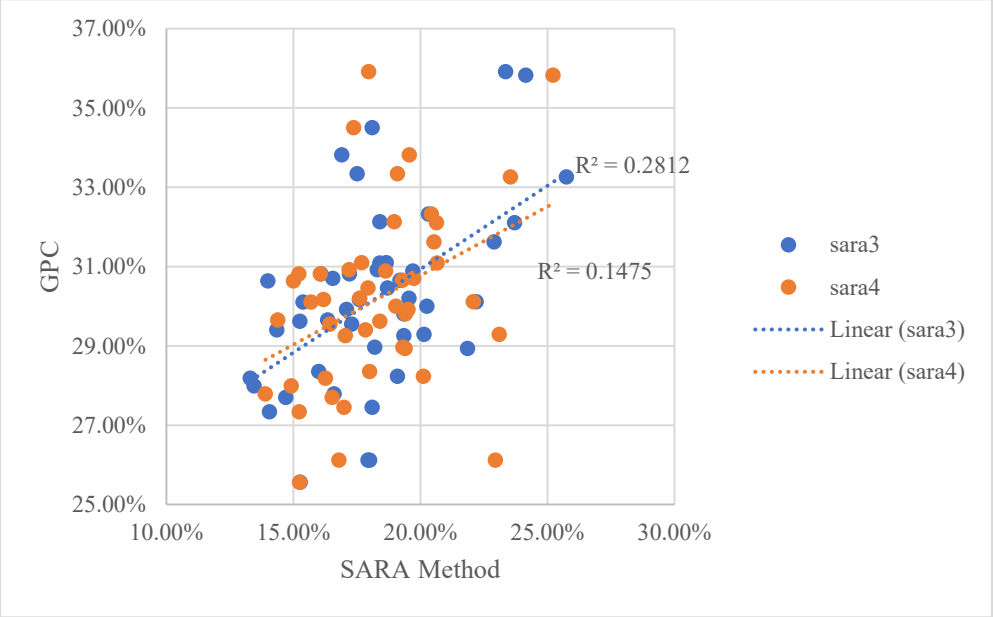
Figure 7 clearly illustrates that GPC consistently reports higher asphaltene values. This can be explained by GPC's reliance on molecular weight for component separation. As shown in the figure, some of the larger maltene molecules fall within the molecular weight range classified as asphaltenes by GPC, resulting in higher asphaltene readings. The average standard deviation of GPC results was 0.52; for the 3-peak method, 0.51; and for the 4-peak method, 0.74.

Regression Between Results

To further evaluate the 3-peak and 4-peak SARA methods with GPC, regression analysis was performed to assess the degree of correlation between each SARA approach and the GPC results. While Figure 8 presents the linear regression outcomes, additional regression models, such as polynomial and logarithmic, were also explored to determine whether variations in PG grade, asphaltene, and maltene content could yield stronger, nonlinear relationships.

Among the models tested, the 3-peak method showed the strongest correlation with GPC using polynomial regression, yielding an R^2 of 0.292. The best correlation for the 4-peak method was obtained with a logarithmic model, yielding an R^2 of 0.15.

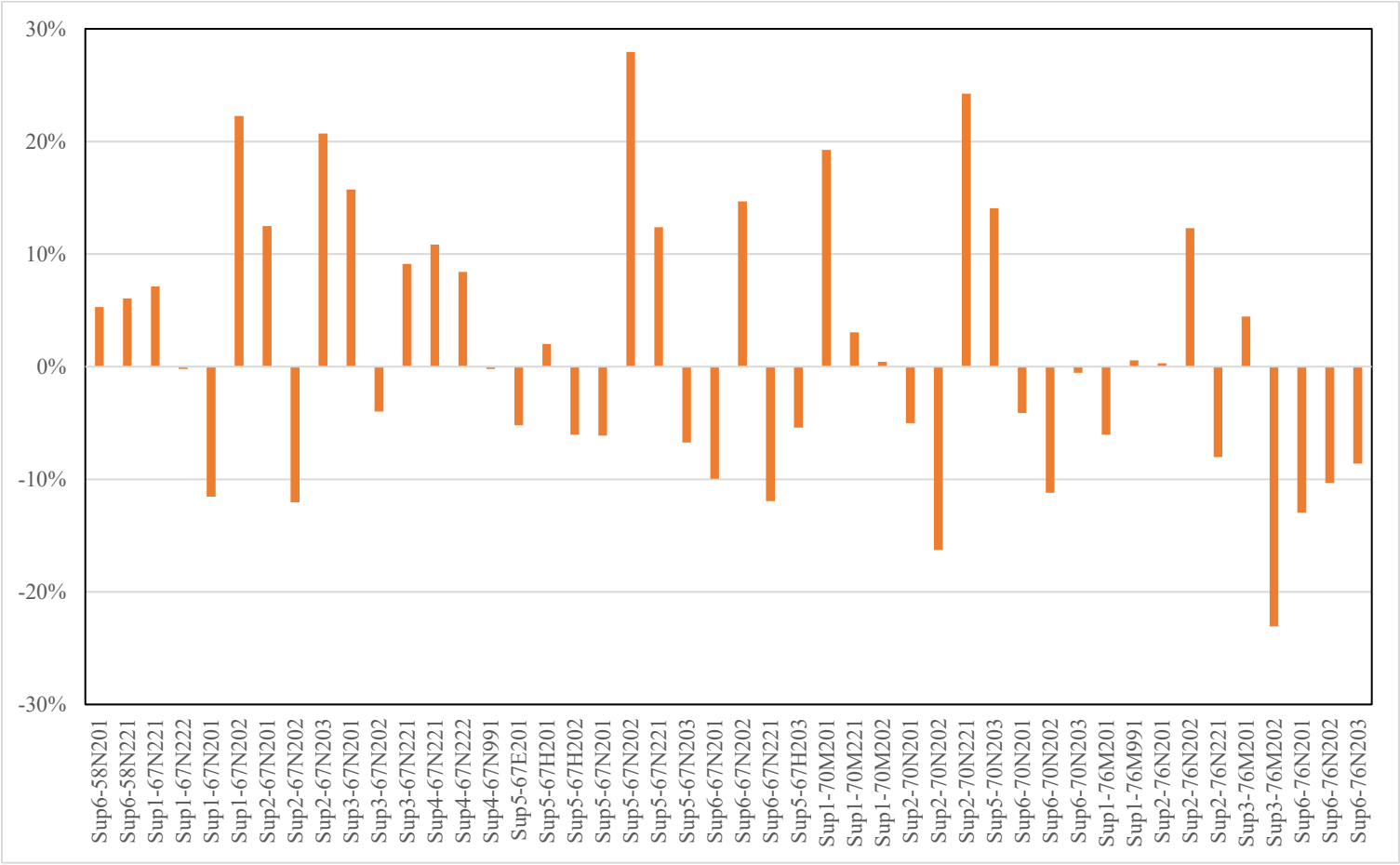
Figure 8. Linear regression between SARA methods and GPC



These findings indicate that the correlation between GPC and the SARA-based methods is generally weak. However, the 3-peak SARA approach showed slightly better alignment with the GPC data than the 4-peak method, suggesting it may more closely reflect GPC's molecular-weight–based component distribution.

To differentiate between the 3-peak and 4-peak methods, the arithmetic differences between the two were analyzed. The percentage differences in asphaltene results obtained from these methods are presented in Figure 9. The maximum difference was observed for Sup5-67N202 (27.94%), and the minimum for Sup3-76M202 (−23.07%). The average magnitude of the deviation between the two methods is 9.55% for the asphalt binders evaluated in this study. While the magnitudes seem comparable, further evaluation is needed to determine the impact of this variation on mixture performance. Additionally, testing efficiency increases notably when using the 4-peak method, as it eliminates the need to separate asphaltenes from the solution.

Figure 9. Arithmetic percent difference between asphaltene results from the 3-peak and 4-peak methods



Statistical Analysis

ANOVA Analysis Between GPC and SARA Grouping

In addition to arithmetic comparison, the test results were evaluated using various statistical methods to assess differences in molecular composition.

A one-way Analysis of Variance (ANOVA) was conducted to analyze the molecular components determined by GPC with those identified using the 3-peak and 4-peak methods of SARA grouping. Since the components determined by GPC differ from those in the SARA grouping, the results are simplified into asphaltene and maltene portions using these test methods. The results indicated significant differences between the molecular components obtained by GPC and those obtained by both the 3-peak and 4-peak SARA methods.

The ANOVA results and corresponding grouping are presented in Table 2, illustrating the statistical significance of the observed differences. The table shows the asphaltene ANOVA grouping, and the maltene results show the same differences, but with the ANOVA grouping reversed.

Table 2. ANOVA analysis of the asphaltene in asphalt binder samples

Binder ID	GPC	Sara3	Sara4
ER67N201	A	B	C
ER67N202	A	C	B
Er67N221	A	B	B
Er67N222	A	B	B
Er70M201	A	C	B
Er70M202	A	B	B
Er70M221	A	B	B
Er76M201	A	B	B
Er76M991	A	B	B
Hd67N201	A	C	B
Hd67N202	A	B	C
Hd67N203	A	C	B
Hd70N201	A	B	B
Hd70N202	A	B	C
Hd70N221	A	C	B
Hd76N201	A	B	B
Hd76N202	A	C	B
Hd76N221	A	B	C

Binder ID	GPC	Sara3	Sara4
Hu67N201	A	C	B
Hu67N202	A	B	B
Hu67N221	A	C	B
Hu76M201	A	B	B
Hu76M202	A	B	C
Mh67N221	A	C	B
Mh67N222	A	B	B
Mh67N991	A	B	B
Mi67E201	A	B	B
Mi67H201	A	B	B
Mi67H202	A	B	B
Mi67H203	A	B	C
Mi67N201	A	B	C
Mi67N202	A	C	B
Mi67N203	A	B	B
Mi67N221	A	B	B
Mi70N203	A	C	B
Va58N201	A	C	B
Va58N221	A	B	B
Va67N201	A	B	C
Va67N202	A	C	B
Va67N221	A	B	C
Va70N201	A	B	B
Va70N202	A	B	C
Va70N203	A	B	B
Va76N201	A	B	C
Va76N202	A	B	B
Va76N203	A	B	C

As shown in Table 2, the GPC results are significantly different from the SARA grouping for each binder evaluated in this study. These results agree with the differences shown in Figure 7. Results from the 3-peak and 4-peak methods show statistically significantly different outcomes in 55% of the samples.

T-test Analysis Between SARA Groupings

A t-test was also performed to compare the molecular components obtained via the 3-peak and 4-peak SARA methods. As summarized in Table 3, the analysis indicated that 55% of the samples exhibited statistically significant differences across all maltene fractions when

comparing the two methodologies. These results suggest a notable lack of statistical agreement between the two SARA approaches across most samples; however, specific instances of variation were observed throughout the dataset.

Table 3. T-test analysis of the maltene components between the 3-peak and 4-peak methods

Binder ID	Variable	t-value	P-value	Difference	Binder ID	Variable	t-value	P-value	Difference
Sup1-67N201	Sat[1]	5.92	<.0001	Sig.[4]	Sup3-67N221	Sat	2.01	0.0675	Not Sig.
	Cyc[2]	-4.06	0.0016	Sig.		Cyc	14.64	<.0001	Sig.
	Res[3]	2.85	0.0146	Sig.		Res	-15.29	<.0001	Sig.
Sup1-67N202	Sat	-1.31	0.2141	Not Sig.[5]	Sup3-76M201	Sat	23.97	<.0001	Sig.
	Cyc	7.84	0.0006	Sig.		Cyc	10.11	<.0001	Sig.
	Res	-6.45	0.0018	Sig.		Res	-14.04	<.0001	Sig.
Sup1-67N221	Sat	3.98	0.0105	Sig.	Sup3-76M202	Sat	2.84	0.0148	Sig.
	Cyc	9.6	<.0001	Sig.		Cyc	10.06	<.0001	Sig.
	Res	-13.79	<.0001	Sig.		Res	-12.57	<.0001	Sig.
Sup1-67N222	Sat	6.11	0.0003	Sig.	Sup4-67N221	Sat	-0.88	0.3971	Not Sig.
	Cyc	3.62	0.0035	Sig.		Cyc	1.15	0.2710	Not Sig.
	Res	-4.93	0.0003	Sig.		Res	-0.84	0.4196	Not Sig.
Sup1-70M201	Sat	0.33	0.7491	Not Sig.	Sup4-67N222	Sat	4.15	0.0013	Sig.
	Cyc	4.14	0.0014	Sig.		Cyc	3.82	0.0024	Sig.
	Res	-4.95	0.0003	Sig.		Res	-4.67	0.0005	Sig.
Sup1-70M202	Sat	0.83	0.4249	Not Sig.	Sup4-67N991	Sat	5.27	0.0051	Sig.
	Cyc	-3.99	0.0021	Sig.		Cyc	9.1	<.0001	Sig.
	Res	2.82	0.0166	Sig.		Res	-11.18	<.0001	Sig.
Sup1-70M221	Sat	2.82	0.0153	Sig.	Sup5-67E201	Sat	9.77	<.0001	Sig.
	Cyc	10.65	<.0001	Sig.		Cyc	1.76	0.1038	Not Sig.
	Res	-10.52	<.0001	Sig.		Res	-4.27	0.0011	Sig.
Sup1-76M201	Sat	-2.65	0.0630	Not Sig.	Sup5-67H201	Sat	1.84	0.1569	Not Sig.
	Cyc	2.99	0.0112	Sig.		Cyc	12.91	<.0001	Sig.
	Res	-0.93	0.3707	Not Sig.		Res	-14.71	<.0001	Sig.
Sup1-76M991	Sat	3.77	0.0027	Sig.	Sup5-67H202	Sat	1.33	0.2072	Not Sig.
	Cyc	3.99	0.0018	Sig.		Cyc	1.15	0.2731	Not Sig.
	Res	-5.94	<.0001	Sig.		Res	1.52	0.1532	Not Sig.
Sup2-67N201	Sat	-2.52	0.0283	Sig.	Sup5-67H203	Sat	1.81	0.1550	Not Sig.
	Cyc	-7.59	0.0004	Sig.		Cyc	9.08	<.0001	Sig.
	Res	8.92	0.0003	Sig.		Res	-10.49	<.0001	Sig.
Sup2-67N202	Sat	2.29	0.0407	Sig.	Sup5-67N201	Sat	1.34	0.2055	Not Sig.
	Cyc	12.25	<.0001	Sig.		Cyc	-4.28	0.0011	Sig.
	Res	-11.85	<.0001	Sig.		Res	3.47	0.0034	Sig.
Sup2-67N203	Sat	-3.8	0.0023	Not Sig.	Sup5-67N202	Sat	-4.71	<.0001	Sig.
	Cyc	0.88	0.3936	Sig.		Cyc	6.03	<.0001	Sig.
	Res	0.53	0.6081	Not Sig.		Res	-3.14	0.0056	Sig.
Sup2-70N201	Sat	-4	0.0018	Sig.	Sup5-67N203	Sat	-0.35	0.7333	Not Sig.

Binder ID	Variable	t-value	P-value	Difference	Binder ID	Variable	t-value	P-value	Difference
Sup2-70N201 (continued)	Cyc	12.52	<.0001	Sig.	Sup5-67N203 (continued)	Cyc	-8.13	0.0004	Sig.
	Res	-12.38	<.0001	Sig.		Res	7.73	<.0001	Sig.
Sup2-70N202	Sat	-1.16	0.3418	Not Sig.	Sup5-67N221	Sat	-22.39	<.0001	Sig.
	Cyc	-0.58	0.5742	Not Sig.		Cyc	14.57	<.0001	Sig.
	Res	0.9	0.3873	Not Sig.		Res	-7.03	<.0001	Sig.
Sup2-70N221	Sat	-2	0.1467	Not Sig.	Sup5-70N203	Sat	2.86	0.0099	Sig.
	Cyc	4.32	0.0119	Sig.		Cyc	14.87	<.0001	Sig.
	Res	-6.71	<.0001	Sig.		Res	-10.94	<.0001	Sig.
Sup2-76N201	Sat	1	0.3408	Sig.	Sup6-58N201	Sat	4.32	0.0010	Sig.
	Cyc	3.18	0.0098	Sig.		Cyc	0.74	0.4722	Not Sig.
	Res	-4.27	0.0016	Sig.		Res	-2.78	0.0167	Significant
Sup2-76N202	Sat	2.19	0.0488	Sig.	Sup6-58N221	Sat	0.89	0.3895	Not Sig.
	Cyc	6.07	<.0001	Sig.		Cyc	8.39	<.0001	Sig.
	Res	-7.27	<.0001	Sig.		Res	-9.14	<.0001	Sig.
Sup2-76N221	Sat	10.44	<.0001	Sig.	Sup6-67N201	Sat	6.3	<.0001	Sig.
	Cyc	2.51	0.0274	Sig.		Cyc	2.23	0.0485	Sig.
	Res	-4.18	0.0013	Sig.		Res	-2.95	0.0169	Sig.
Sup3-67N201	Sat	19.82	<.0001	Sig.	Sup6-67N202	Sat	-4.54	0.0007	Sig.
	Cyc	10.35	<.0001	Sig.		Cyc	-0.25	0.7806	Not Sig.
	Res	-21.37	<.0001	Sig.		Res	0.84	0.3637	Not Sig.
Sup3-67N202	Sat	0.7	0.4963	Not Sig.	Sup6-67N221	Sat	9.35	<.0001	Sig.
	Cyc	3.4	0.0053	Sig.		Cyc	-1.6	0.1359	Not Sig.
	Res	-4.8	0.0004	Sig.		Res	-1.6	0.1355	Not Sig.
Sup6-76N201	Sat	5.97	<.0001	Sig.	Sup6-70N201	Sat	5.33	0.0002	Sig.
	Cyc	2.17	0.1035	Not Sig.		Cyc	10.11	<.0001	Sig.
	Res	-8.88	<.0001	Sig.		Res	-16.07	<.0001	Sig.
Sup6-76N202	Sat	0.97	0.3520	Not Sig.	Sup6-70N202	Sat	-5.91	0.0017	Sig.
	Cyc	-1.92	0.0756	Not Sig.		Cyc	20.31	<.0001	Sig.
	Res	1.91	0.0832	Not Sig.		Res	-20.65	<.0001	Sig.
Sup6-76N203	Sat	0.83	0.4231	Not Sig.	Sup6-70N203	Sat	-10.79	<.0001	Sig.
	Cyc	0.64	0.5348	Not Sig.		Cyc	14.38	<.0001	Sig.
	Res	-0.84	0.4153	Not Sig.		Res	-12.37	<.0001	Sig.

[1] Saturates

[2] Cyclics and Aromatics

[3] Resins

[4] Significant

[5] Not Significant

Effect of Binder Source on Asphalt Binder Components

GPC Components of PG 67-22

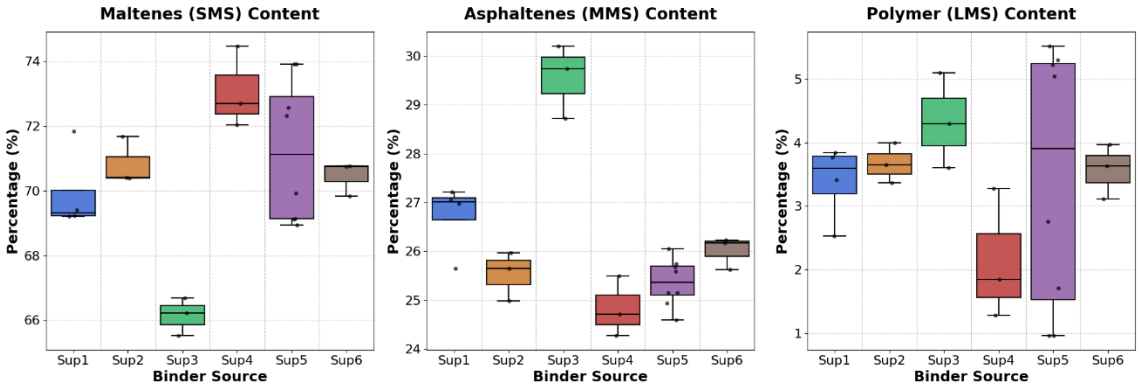
Figure 10 illustrates the variation of GPC fractions for PG 67-22 from different sources.

Maltenes (SMS—Small Molecular Size): The PG 67-22 binders show clear differences in maltene content across sources. The Sup4 binders are at the top, with the highest average fraction of lighter components at approximately 73%. The Sup5 and Sup2 sources follow closely, though the Sup5 data is more scattered. The Sup3 binders are the distinct outliers, carrying a much lower SMS fraction that averages around 66%. Since the Sup4 source is rich in these smaller molecules, it likely disperses polar asphaltenes better than the others. While this usually helps with workability (i.e., lower initial viscosity), there is a trade-off: lighter oils are often more volatile. This observation means the Sup4 binder could oxidize and harden faster than the "heavier" Sup3 source. It is noted that GPC only separates by size, not solubility or polarity; therefore, it cannot strictly distinguish which parts of the maltene fraction are reactive [7] [8] [9] [10].

Asphaltenes (MMS—Medium Molecular Size): As expected, the Medium Molecular Size fraction shows an inverse relationship to the maltenes. The Sup3 source exhibited the highest average MMS content (≈30%), pointing to a binder with a more highly structured internal network or significant molecular agglomeration. Conversely, Sup4 displayed the lowest MMS content. This observation suggests that the Sup3 source likely derives its PG 67 grade stiffness primarily from these natural asphaltene-like structures, whereas the lighter Sup4 source relies less on other molecular components to build stiffness [7] [8] [9] [10].

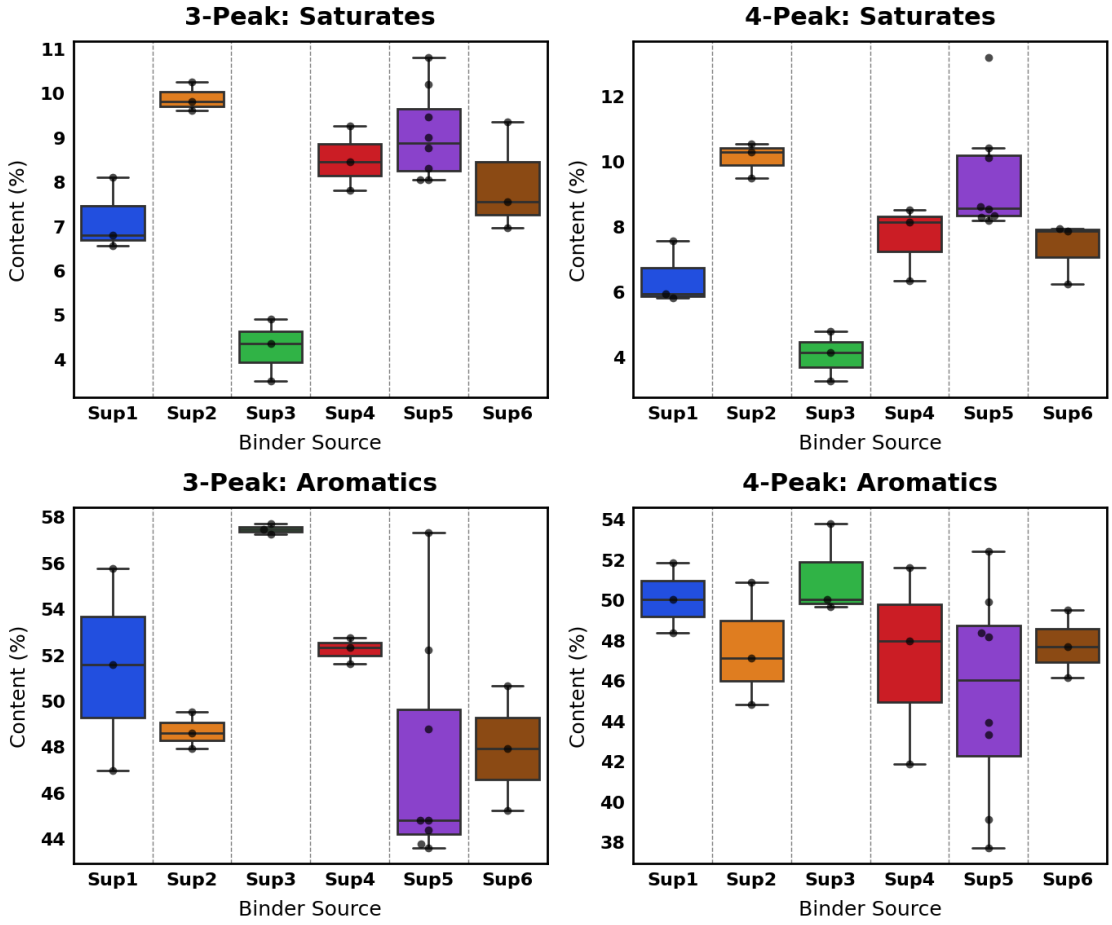
Polymer (LMS—Large Molecular Size): All sources showed negligible average LMS values (< 4.5%), consistent with the profile of unmodified PG 67-22 binders. While Sup5 showed the widest variability, ranging from ≈1.0% to 5.5%, and Sup3 consistently hovered on the higher end, these values likely represent the heavy "tail end" of the asphaltene distribution rather than actual polymer modification. To truly understand the practical implications of these molecular variations, rheological and mechanical testing of the binders is necessary. Historically, binders with a high degree of asphaltene association, such as those seen in the Sup3 source, tend to exhibit high stiffness but limited ability to relax stress, making them more prone to thermal and fatigue cracking [7].

Figure 10. GPC components for PG 67-22 from different sources



SARA analysis of asphalt binders separates components by polarity and solubility, offering a clearer chemical fingerprint. Figure 11 presents box plots of saturates and aromatic components for PG 67-22 asphalt binders from different sources.

Figure 11. Saturate and aromatic components for PG 67-22



Saturates: The SARA saturate fraction proved to be a useful, albeit variable, fingerprinting tool for the PG 67-22 asphalt binders. The data revealed that while identifying extreme outliers was possible, distinguishing between the majority of sources was challenging due to overlapping ranges. The Sup2 and Sup5 binders appeared chemically distinct at the high end, exhibiting the highest average saturate contents (approximately 10% and 9.5%, respectively). In contrast, the Sup3 binder was distinct at the low end, averaging 4.0%. However, for the intermediate sources (Sup1, Sup4, Sup6), there was no practically significant difference; their values clustered closely, with substantial overlap, making it difficult to fingerprint these sources based on saturates alone.

From a performance perspective, the high saturate content observed in Sup2 and Sup5 often indicates a paraffinic nature. Paraffins are prone to crystallization at low temperatures, which can induce physical hardening and minimize stress relaxation capabilities. Further, because saturates are non-polar, they can compromise adhesion to aggregates, thereby increasing the

pavement's susceptibility to moisture damage (i.e., stripping) [11] [12] [13]. While increasing the saturate content, despite maintaining a constant resin-to-aromatic ratio, may have softened the bitumen, it also likely contributed to the binder's gel character [14]. Consequently, despite sharing the same Performance Grade, the high-saturate Sup2 and Sup5 binders theoretically posed a higher risk of low-temperature cracking than the Sup3 source. The two SARA techniques (3- and 4-peak methods) showed relatively consistent saturate fractions.

Aromatics: Aromatics provide the necessary dispersion medium for polar resins and asphaltenes, preventing agglomeration and maintaining a stable colloidal structure. The Sup3 source consistently displayed the highest average aromatic content across both test methods (3-Peak: 57.5%; 4-Peak: 51.1%). This suggested a crude source naturally rich in aromatics, which generally helps soften the binder and minimize shear susceptibility. However, aside from the Sup3 source, there was a notable lack of practically significant difference among the remaining binders (Sup1, Sup2, Sup4, Sup5, Sup6). As shown in the box plots, these sources clustered in an intermediate range (47 to 52%) with significant overlap. The Sup5 source showed a particularly wide variance in the 4-peak method, nearly spanning the entire range of other binders. This overlap confirmed that for the majority of these sources, the aromatic fraction was not a reliable fingerprinting metric.

A distinct systematic bias was observed between the two measurement techniques regarding aromaticity. The 3-peak method consistently reported higher aromatic values (mean = 51%) than the 4-peak method (mean = 48%). This discrepancy was likely attributable to the manual filtration step in the 3-peak method, where the use of n-heptane may have caused some polar resins to associate with the aromatic fraction during development. Alternatively, the single chromatographic column used in the 4-peak method may have lacked the resolution required to fully separate complex binders with extensive polarity ranges, potentially blurring the resin/aromatic boundary in-situ [15] [16].

Figure 12 shows the box plots for resin and asphaltene components for the PG 67-22 asphalt binders.

Resins: Resins act as critical peptizing agents, dispersing asphaltenes within the oily maltene phase and largely governing the binder's sol-gel properties. Among the evaluated binders, the Sup4 and Sup1 sources displayed the highest average resin fractions, a trend particularly evident in the 4-peak method, where values approached 30%. However, there was no practically significant difference among the Sup4, Sup1, Sup6, and Sup5 sources in the 4-peak method due to substantial overlap in data distributions. The Sup5 source exhibited a

particularly wide range (approximately 22 to 35%), encompassing the values of other high-resin binders. Consequently, fingerprinting most sources based solely on resin content using the 4-peak method appears unreliable. The Sup3 source was a notable exception, exhibiting comparatively lower resin content, particularly in the 3-peak method (21.2%).

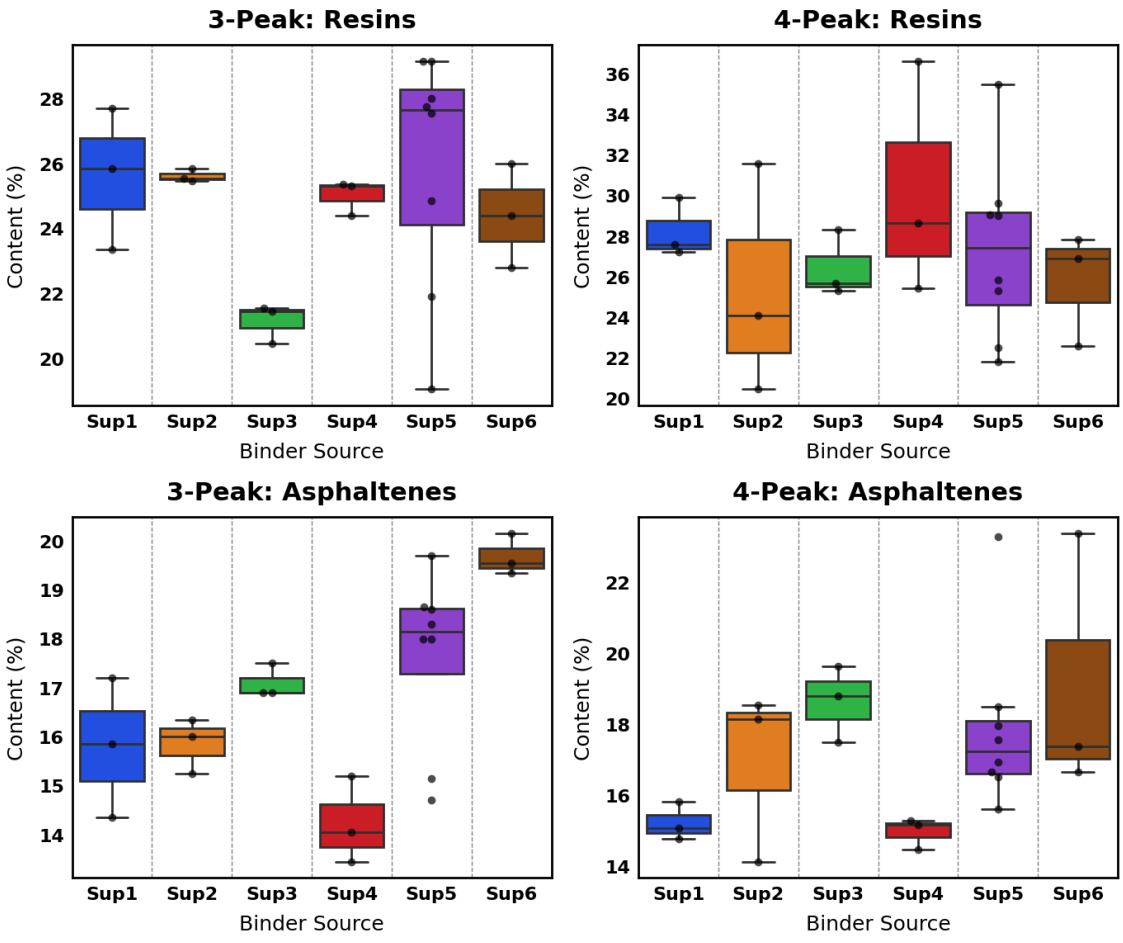
The 4-peak method consistently yielded higher average resin values (+1% to +5%) than the 3-peak method. This systematic difference confirms that the in-situ chromatographic separation of the 4-peak method classifies a broader spectrum of polar molecules as resins. In contrast, the physical filtration required by the 3-peak method likely groups some of these borderline polar species with aromatics or asphaltenes [16] [17]. This finding aligns with that of Jiang et al. [18], which demonstrated that comparing 4-peak data to conventional gravimetric methods is problematic for crude oils with high polar content. Conventional precipitation often occludes resins within the asphaltene fraction, creating discrepancies because the two methods rely on fundamentally different separation mechanisms. To clarify these mechanistic differences, specifically regarding asphaltenes that are not obtained via precipitation, Masson et al. [19] proposed the terminology SARAB for TLC-FID: saturates, aromatics, resins A (eluted by tetrahydrofuran), and resins B (uneluted residue at the origin).

Further, the higher resin content observed in the 4-peak method may be attributed to experimental variables identified by Masson et al. [19]. Their research indicates that chromarod aging (usage > 60 times) causes surface deactivation, leading to a 2 to 5% statistical variation characterized by an apparent increase in polar fractions (resins A and B) at the expense of non-polar fractions. Additionally, the time lapse between binder dissolution and analysis significantly impacts results; extended solution time can induce a conversion of aromatics into resins A, potentially causing variations of 50 to 75% in these fractions [19].

Asphaltenes: Asphaltenes are the most polar and viscous components of bitumen, serving as the agents that primarily define the binder's stiffness and elastic recovery. The Sup6 and Sup3 sources exhibited the highest average asphaltene content (Sup6: ≈19.7% in 3-peak; Sup3: ≈18.7% in 4-peak). This data suggested that these specific binders relied more heavily on a rigid asphaltene structural network to achieve the stiffness required for the PG 67 grade. Conversely, the Sup4 source consistently showed the lowest asphaltene content (≈14–15%), implying it was a lighter binder that likely relied on a viscos maltene phase to meet grade specifications [7] [8] [9] [10] [11]. However, for the remaining sources (Sup1, Sup2, and Sup5) there was a distinct lack of practically significant difference. These binders fell into an intermediate cluster (15 to 18%) with overlapping error bars, making them indistinguishable based on asphaltene content alone.

Regarding the test methods, the Sup6 source presented a notable exception to the general trends. While the 4-peak method generally reported slightly higher asphaltene values for most sources (e.g., Sup3 was ≈1.5% higher in 4-peak), the Sup6 binders showed lower asphaltenes in the 4-peak method compared to the 3-peak method. This source-dependent bias indicated that the chemical nature of the asphaltenes, specifically their polarity and solubility, varied significantly by source. The Sup3 asphaltenes appeared to be more polar or stickier, retaining firmly to the origin of the 4-peak chromarod. Sup6 asphaltenes, however, appeared to be slightly more soluble; in the 4-peak method (i.e., chromatographic retention), these marginally soluble species migrated further up the rod and were reclassified as resins, whereas the 3-peak method (i.e., physical filtration) captured them as insoluble [16] [17]. Jiang et al. found the comparison between the 3- and 4-peak SARA components to be problematic, as the two techniques rely on different separation mechanisms [18].

Figure 12. Resin and asphaltene components for PG 67-22

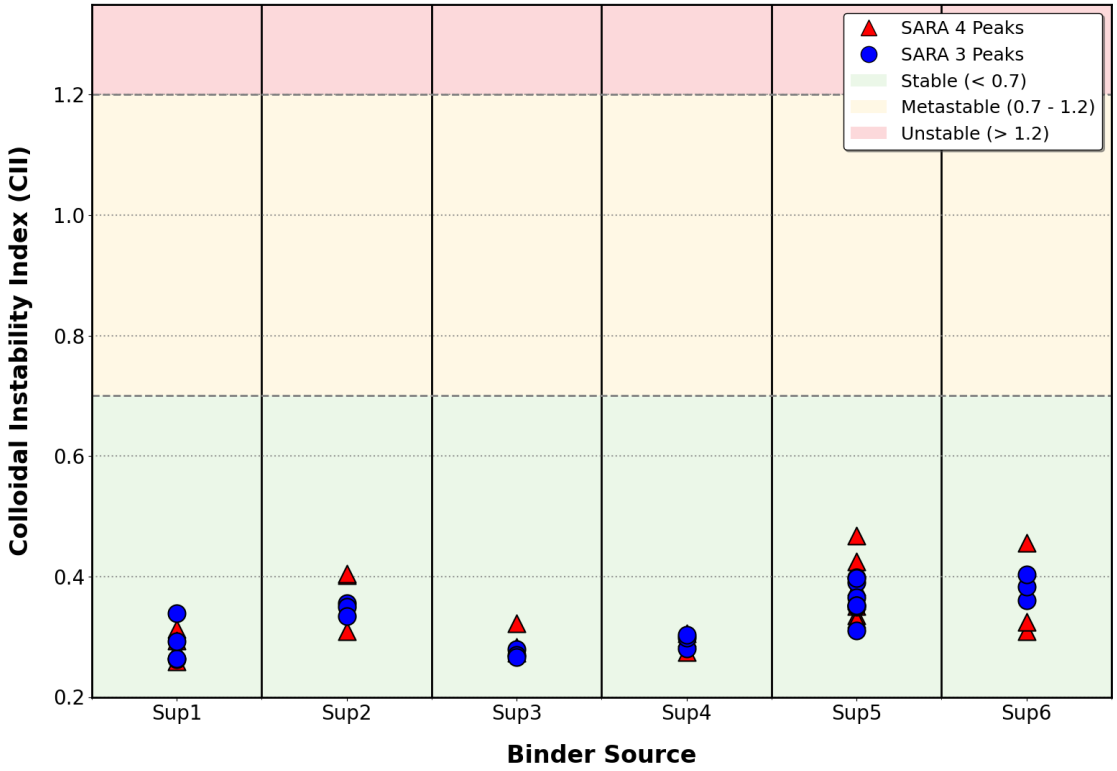


Generally, the SARA analysis (both 4-peak and 3-peak methods) reliably distinguished PG 67-22 binder sources based on their saturate content, indicating paraffinicity, and the specific balance between aromatics and resins. The 4-peak method is generally preferred over the 3-peak method as it offers equivalent discriminatory power while being significantly faster due to the elimination of the manual filtration step. While GPC proved useful for confirming the absence of polymers (LMS) and distinguishing between heavy and light crude sources via the maltene/asphaltene ratio, it remained less specific regarding chemical polarity or solubility than SARA [7] [8] [9] [10] [11].

Colloidal Instability Index: Asphalt functions as a dispersion of asphaltene micelles suspended in an oily maltene medium. For the system to remain stable, the resin and aromatic fractions must provide sufficient solvent power to keep the asphaltenes dispersed. If this solvent power is inadequate, due to excessive saturates or insufficient aromatics, the asphaltenes will agglomerate into large networks. This creates “gel” characteristics, leading to oil exudation and reduced pavement durability [7] [8] [9] [10] [11].

Figure 13 presents the CII values for PG 67-22 binders from various sources. The CII, calculated as the ratio of flocculants (saturates + asphaltenes) to peptizers (resins + aromatics), serves as a primary indicator of colloidal stability. Higher values indicate a “gel-type” structure prone to phase separation. As shown in the plot, the PG 67-22 binders from every source (Sup1, Sup2, Sup3, Sup4, Sup5, Sup6) fall clearly within the stable (sol-type) zone, with values ranging from 0.26 to 0.47. Despite minor variations, none of these unmodified binders approached the metastable or sol-gel threshold (0.7), let alone the higher values associated with severe gelation or flocculation risks. The binders exhibit a well-peptized structure where the asphaltenes are effectively dispersed by the aromatic/resin matrix [14] [20] [21] [22]. Further, the 3-peak and 4-peak methods demonstrate strong agreement, with data points for each source clustering closely; this confirms that either method is valid for determining the stability classification of these binders.

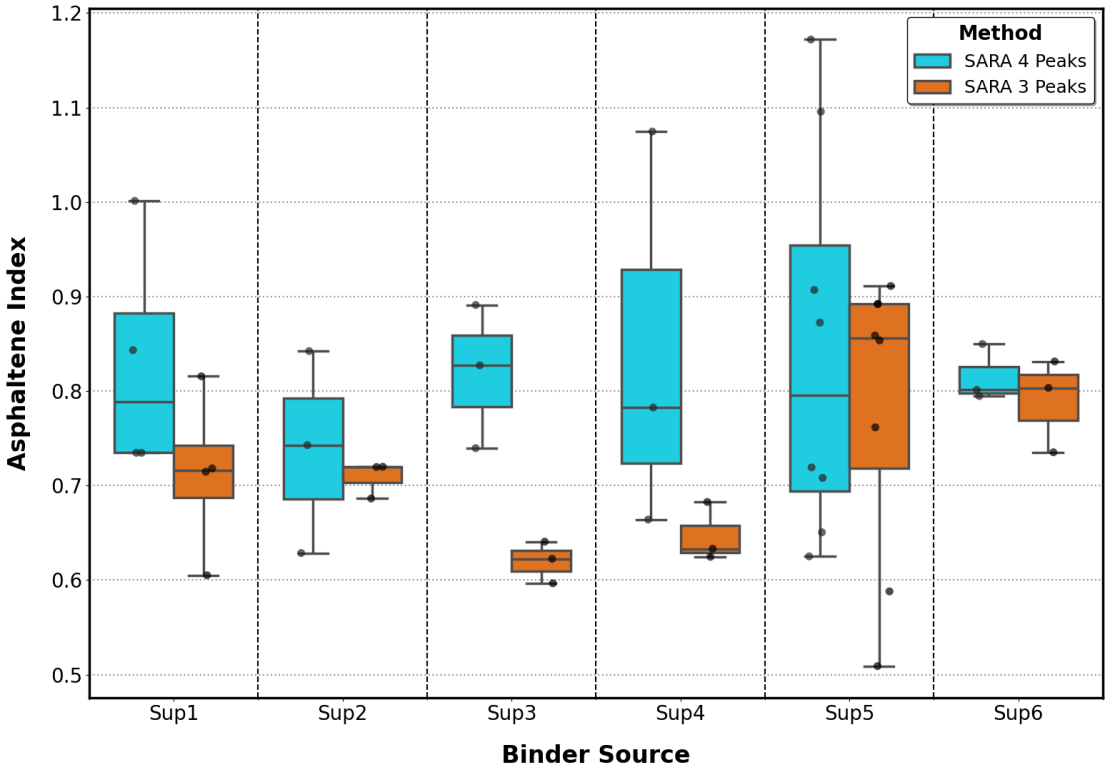
Figure 13. CII for PG 67-22 asphalt binders



Asphaltene Index (AI): Figure 14 illustrates the distribution of AI values for PG 67-22 binders across various sources. Generally, the AI served as a proxy for binder stability [21] [22], quantifying the ratio of asphaltenes to the maltene phase components. The Sup5 source appeared to exhibit the highest average AI values (4-peak: ≈0.87; 3-peak: ≈0.85). However, as indicated by the wide error bars in the plot, this source displayed significant variability. Consequently, there was substantial overlap among the distributions of the Sup1, Sup2, and Sup5 sources. This overlap indicated a lack of practically significant difference between these binders, limiting the ability to fingerprint these specific sources based solely on the Asphaltene Index. A striking discrepancy appeared in the Sup3 source: it recorded a relatively high AI under the 4-peak method (≈0.82) but dropped to the lowest AI using the 3-peak method (≈0.62). This sharp contrast suggested that the 3-peak filtration process likely removed a specific fraction of polar material that the 4-peak method retained and counted as asphaltenes. Meanwhile, the Sup6 binder maintained consistently similar AI values across both techniques, showing less sensitivity to the method used. On average, the 4-peak method yielded higher AI values (mean ≈0.81) compared to the 3-peak method (mean ≈0.71). This systematic offset implied that the 4-peak method defined asphaltenes more broadly, capturing

a wider range of polar components, which may complicate direct comparisons with historical data derived from traditional precipitation-based methods [21] [22].

Figure 14. AI plots for PG 67-22 asphalt binders



CII proved to be a robust parameter for characterizing PG 67-22 binder sources. While all binders remained within the stable range, the index effectively stratified those with relatively higher instability indices (Sup5, Sup2, Sup6) from the highly stable sources (Sup1, Sup3, Sup4). In contrast, the AI was significantly more sensitive to the specific test method used.

Effects of Binder Source on GPC Components: PG 70-22

Figure 15 illustrates the variation of GPC fractions for PG 70-22 from different sources.

Maltenes (SMS—Small Molecular Size): For the PG 70-22 asphalt binders, the Sup2 source exhibited the highest average maltene content, averaging roughly 71%. The Sup6 and Sup5 binders followed closely behind, hovering near 70%. In contrast, the Sup1 binders sat at the lower end of the spectrum (≈69%). It is noted that minor differences in maltene content among the asphalt binders may not be practically significant, as they are likely within the

testing device's error range. A higher SMS fraction, as seen in the Sup2 samples, suggests potentially better flow properties at low temperatures, but it often comes with a trade-off: greater susceptibility to oxidative aging and volatilization [7] [8] [9] [10].

Asphaltenes (MMS—Medium Molecular Size): The Sup1 source displayed the highest average MMS content (25.7%), confirming it uses a heavier, more structured base binder than Sup2, which had the lowest average at approximately 24.0%. This higher MMS content in the Sup1 samples likely provides more natural stiffness and rutting resistance from the asphalt cement itself, independent of the polymer modification [7] [8] [9].

Polymer (LMS—Large Molecular Size): All sources showed a distinct polymer peak, with values generally ranging from 4.3% to 6.0%. This confirms that every sample tested is modified with elastomeric polymers (likely SBS) to achieve the PG 70-22M grade. The consistency of this peak makes GPC an effective tool for verifying that the binder is modified, though it is less useful for distinguishing between the sources themselves.

Ultimately, the GPC test confirms all binders are polymer-modified, distinguishing the sources primarily by their base chemistry: Sup2 is a lighter base (high maltenes/SMS), while Sup1 is a heavier base (high asphaltenes/MMS) [7] [8] [9] [10] [11].

Figure 15. GPC components for PG 70-22 asphalt binders

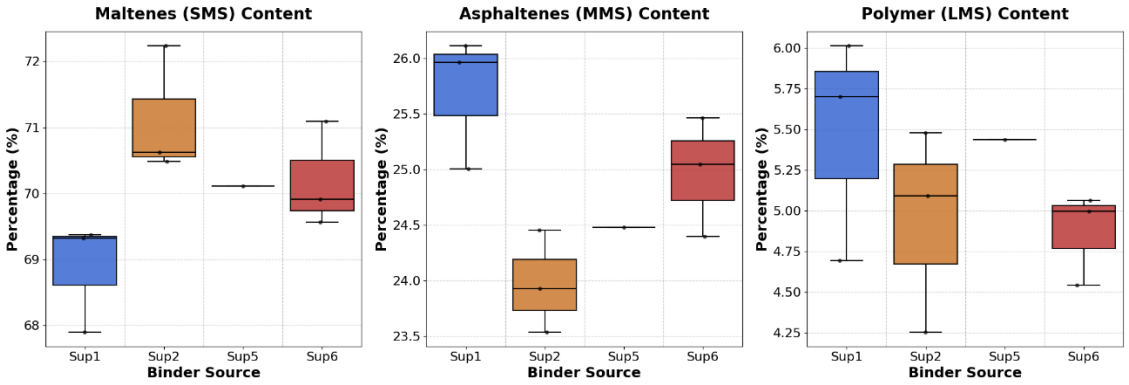


Figure 16 presents box plots for saturate and aromatic components for PG 70-22 asphalt binders from different sources.

Saturates: The Sup5 sample exhibited the highest saturate content in the 3-peak method (10.5%), while the Sup2 displayed the highest average content in the 4-peak method (10.4%). Despite this ranking shift, Sup2 consistently tracked as a high-saturate source, averaging 9.5% in the 3-peak method and 10.4% in the 4-peak method, serving as a robust marker of a

more paraffinic crude origin. In contrast, Sup1 and Sup6 tracked lower. Sup6 averaged 8.9% (4-peak) and 8.4% (3-peak), while Sup1 averaged 7.9% (4-peak) and 8.3% (3-peak). The data indicated considerable overlap between these lower-saturate sources, suggesting that there was no practical significant difference between Sup1 and Sup6 regarding their paraffinic content. Overall, the 4-peak method appeared more effective for the saturate fraction because it aligned Sup2's high paraffin content more consistently with its known material properties from the GPC test.

Aromatics: Sup6 exhibited the highest average aromatic content across both methods (mean: 53.1% in 3-peak; 47.5% in 4-peak). However, the data revealed that the differences between the top three sources were marginal in the 4-peak method; Sup6 (47.5%), Sup2 (46.7%), and Sup1 (46.5%) were separated by only 1.0%, indicating that the variation was practically insignificant. This observation points to crude sources naturally rich in aromatic oils. Conversely, Sup5 showed the distinct lowest aromatic content, particularly in the 4-peak method, where it dropped to 41.5%. This leaner solvent matrix implied the binder relied more heavily on its resin fraction for colloidal stability.

From a performance standpoint, the high aromaticity observed in Sup6, and practically shared by Sup1 and Sup2 in the 4-peak data, suggested a superior capacity to keep asphaltenes dispersed. This dispersion offers better short-term resistance to age hardening (i.e., gelation). However, because aromatics are the first fraction consumed during oxidative aging, this advantage may diminish over time. While high aromatics support bulk stability, if they overpower the resins, it might reduce the binder's tackiness or adhesion properties compared to the resin-rich Sup5 [11] [12] [13] [14]. Comparing the two techniques, the 4-peak method demonstrated superior discrimination. It provided the clearest separation between the uniquely low-aromatic Sup5 sample and the group of higher aromatic sources, whereas the 3-peak method compressed the data, making the distinction between Sup5 (48.7%) and Sup1 (49.4%) less clear.

Figure 16. Saturate and aromatic components for PG 70-22 from different sources

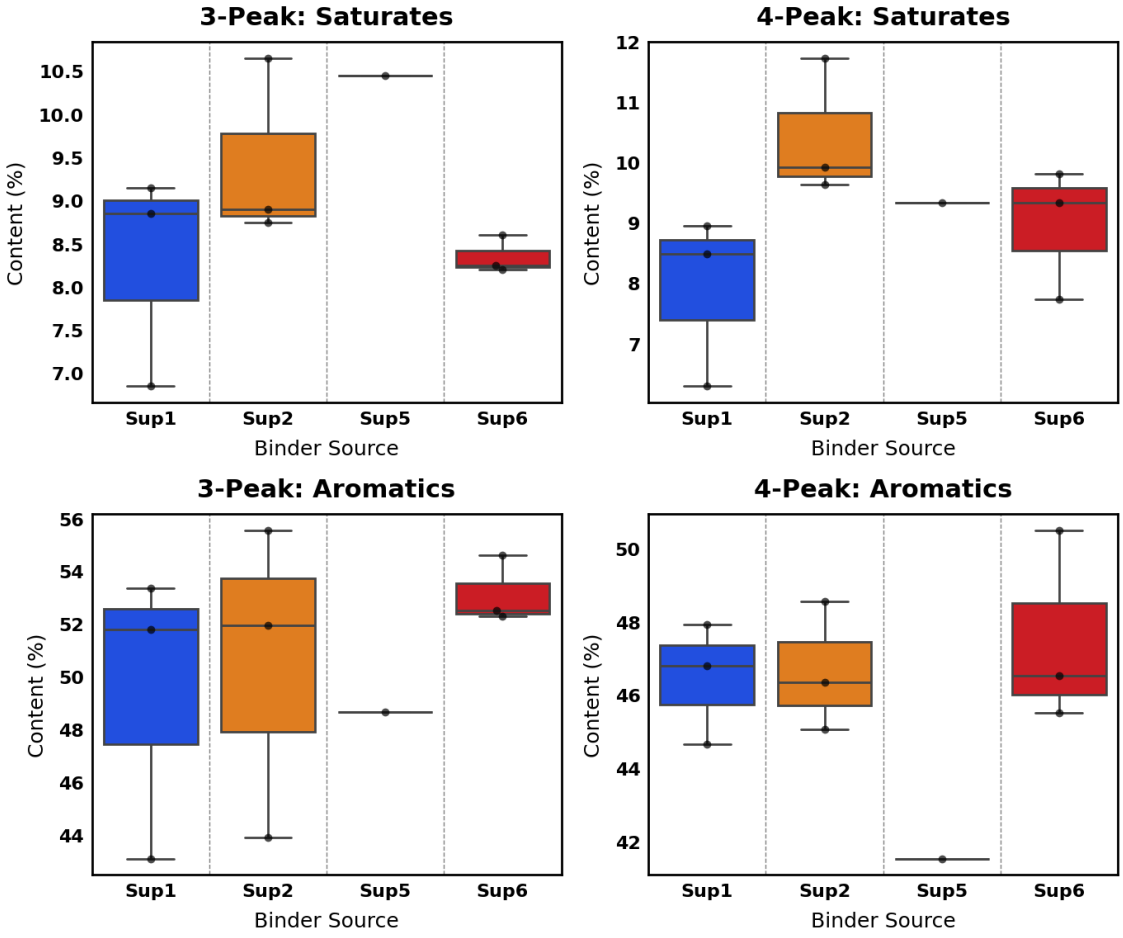


Figure 17 presents box plots for resin and asphaltene components for PG70-22 asphalt binders from different sources.

Resins: Sup5 exhibited the highest resin content in the 4-peak method, reaching 29.5%. This high resin load appears to compensate for the binder's low aromaticity, ensuring stability through strong peptization. At the other end of the spectrum, Sup6 consistently showed the lowest resin content (mean: 17.6% in 3-peak; 23.8% in 4-peak). This confirms that Sup6 relies primarily on solvency (aromatics) rather than peptization (resins) to maintain its structure. Sup2 and Sup1 fall in the middle, showing moderate to high resin levels (approximately 26 to 27% in the 4-peak method), which suggests a chemically balanced stabilizing system. From a performance standpoint, Sup5's high resin content suggests it acts as a robust "sol-type" binder, with asphaltenes heavily solvated. This structure is generally more resistant to oxidative embrittlement (i.e., cracking) because the abundant resins provide a buffer against the formation of new asphaltenes. Since resins contribute significantly to

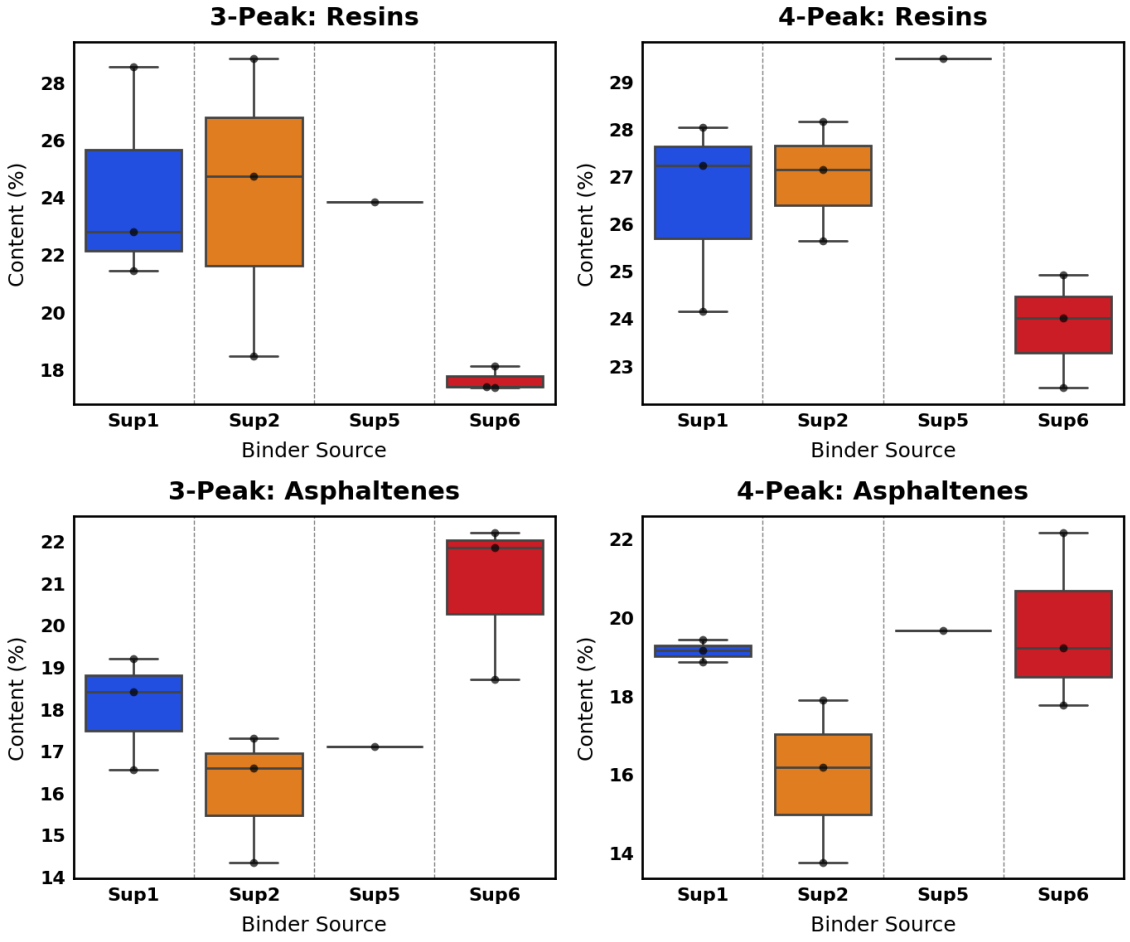
viscoelastic properties and adhesion, the Sup5 and Sup1 binders may exhibit better aggregate adhesion and elastic recovery compared to the resin-poor Sup6 binder [11] [12] [13] [14].

Methodologically, the 4-peak method consistently yielded higher resin values (+2% to +6%) than the 3-peak method, confirming the earlier observation from the aromatics analysis. The 4-peak method captures a broader range of polar molecules as resins, likely including semi-polar species that were lost to the aromatic fraction in the 3-peak n-heptane separation. For polymer-modified binders like these, the 4-peak method is arguably superior, as it avoids the physical entrapment of resins in the polymer-asphaltene filter matrix that can occur during 3-peak filtration [16] [17].

Asphaltenes: Sup5 showed the highest resin content by the 4-peak method, at 29.5%. This high resin load appeared to compensate for the binder's low aromaticity, ensuring stability through strong peptization. In the 3-peak method, Sup2 showed the highest average (28.7%), though the difference between Sup2 and Sup5 was practically insignificant. At the other end of the spectrum, Sup6 consistently showed the lowest resin content (mean: 17.6% in 3-peak; 23.8% in 4-peak). This confirmed that Sup6 relied primarily on solvency (aromatics) rather than peptization (resins) to maintain its structure. Sup2 and Sup1 fell in the middle range for the 4-peak method (averaging approximately 27% and 26.5%, respectively). The box plots and averages indicated significant overlap between Sup2 and Sup1 in the 4-peak method, suggesting chemically balanced stabilizing systems with no practical significant difference between them. From a performance standpoint, Sup5's high resin content suggested it acted as a robust sol-type binder, with asphaltenes heavily solvated. This structure is generally more resistant to oxidative embrittlement (i.e., cracking) because the abundant resins provide a buffer against the formation of new asphaltenes. Since resins contribute significantly to viscoelastic properties and adhesion, the Sup5 and Sup1 binders were expected to exhibit better aggregate adhesion and elastic recovery compared to the lower resin content Sup6 binder. [11] [12] [13] [14] [15] [17].

Comparing the two fractionation techniques, the 4-peak method consistently yielded higher resin values (+2% to +6%) than the 3-peak method. The 4-peak method appeared to be superior for this fraction, as it avoided the physical entrapment of resins in the polymer-asphaltene filter matrix that can occur during 3-peak filtration. It also provided a clearer distinction for the unique Sup5 source, whereas the 3-peak method blurred the distinction between Sup2 and Sup5 [16] [17].

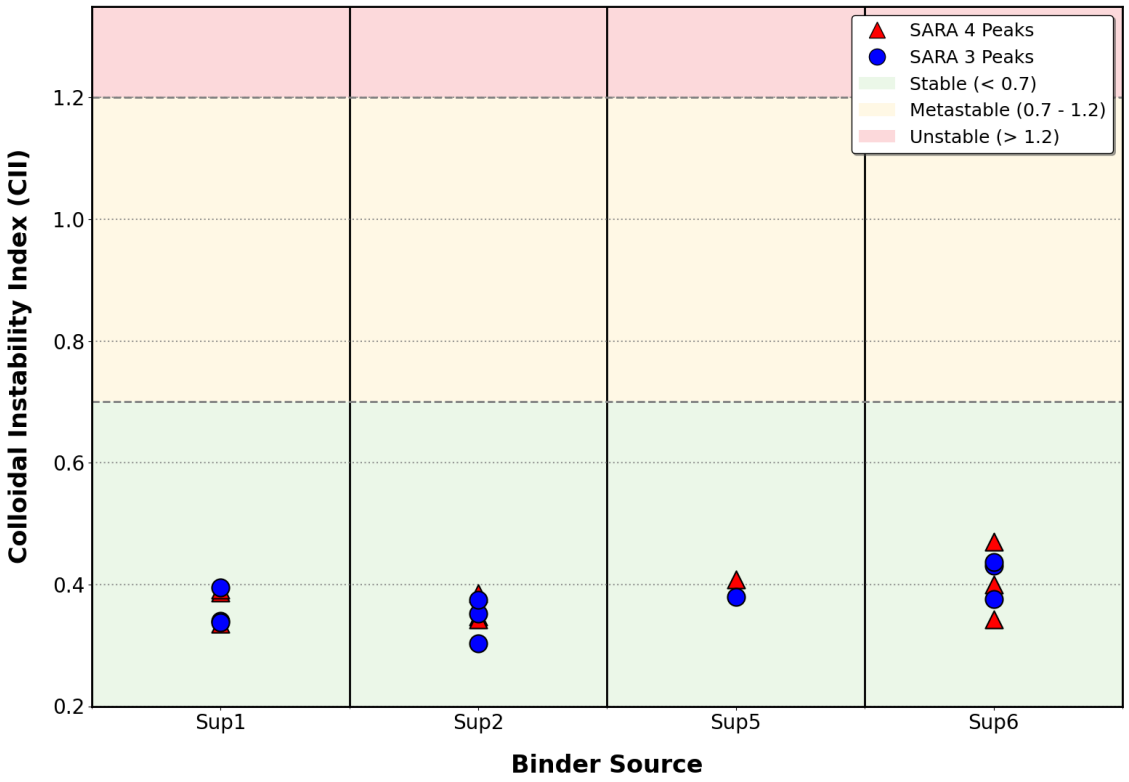
Figure 17. Resin and asphaltene components for PG 70-22 from different sources



Colloidal Instability Index: Figure 18 presents the CII values for the PG 70-22 asphalt binders from different sources. All PG 70-22M binders (Sup1, Sup2, Sup5, Sup6) exhibited CII values ranging broadly from 0.30 to 0.47. Notably, every single data point fell well within the stable (sol-type) zone (CII < 0.7), indicated by the green band in the figure. The differences observed between the sources were mostly insignificant. While slight numerical variations existed, with Sup6 and Sup5 trending slightly higher and Sup2 slightly lower, these distinctions were negligible in the context of overall colloidal stability. All binders were positioned deep within the stable region, well below the metastable threshold (0.7). Consequently, all sources demonstrated a robust sol-type structure in which asphaltenes were effectively dispersed by the solvent matrix and the polymer network.

Both the 3-peak and 4-peak methods showed strong agreement in classifying all binders as stable. The minor variations observed were methodological rather than structural.

Figure 18. CII values for PG 70-22 asphalt binders



Asphaltene Index (AI): The Sup5 source exhibited the distinct highest AI in the 4-peak method (0.966), measuring significantly higher than all other sources. However, in the 3-peak method, the value dropped sharply to 0.693, placing it in the middle range of the dataset. This massive discrepancy suggested that the asphaltenes defined by the 4-peak method for the Sup5 source included a significant fraction of polar material that was soluble in n-heptane, and thus filtered out in the 3-peak method. Consequently, this source appeared chemically unique, possessing a very high concentration of borderline polar molecules [16] [17]. Sup1 consistently ranked second-highest in the 4-peak method (mean: 0.840). However, in the 3-peak method, Sup1 dropped (mean: 0.650), and the data range overlapped significantly with Sup6, indicating that there was no practically significant difference between Sup1 and Sup6 using the conventional 3-peak parameter. Sup6 and Sup2 displayed the lowest ranges in the 4-peak method (means of 0.771 and 0.753, respectively). The overlap between them was substantial, indicating they were practically indistinguishable regarding this metric in the 4-peak method. Conversely, the 3-peak method produced highly variable results for Sup2 (mean: 0.796, but with individual values ranging wildly from 0.64 to 0.91), making it difficult to confidently rank it against the consistently lower Sup6 (mean: 0.627).

From a performance perspective, a higher AI, as consistently seen in Sup1 and Sup5 via the 4-peak method, generally correlated with higher stiffness and elastic recovery. This structural rigidity enhances rutting resistance. However, if the AI becomes too high (approaching 1.0, as seen with Sup5), the binder risks becoming overly structured. Without a sufficient maltene phase to plasticize these structures, the binder may become brittle and prone to cracking at low temperatures. The lower AI values in Sup6 and Sup2 indicated a more maltene-rich or solvated system, likely offering better relaxation properties but potentially lower resistance to permanent deformation [21] [22].

The 4-peak method appeared significantly more effective for analyzing the Asphaltene Index in these polymer-modified binders. It consistently yielded higher AI values (+0.07 to +0.27) than the 3-peak method, confirming that it captures a broader definition of asphaltenes, likely including heavy resins, that contribute to the binder's rheological structure. Notably, the 4-peak method provided stable, distinct groupings, separating Sup5 and Sup1 from Sup6 and Sup2, whereas the 3-peak method suffered from extreme variance, particularly with Sup2, and failed to distinguish the chemically unique Sup5 source from the average. For polymer-modified binders, the 4-peak method offered a better representation of the effective polar structure.

Figure 19. AI plots for PG 70-22 asphalt binders

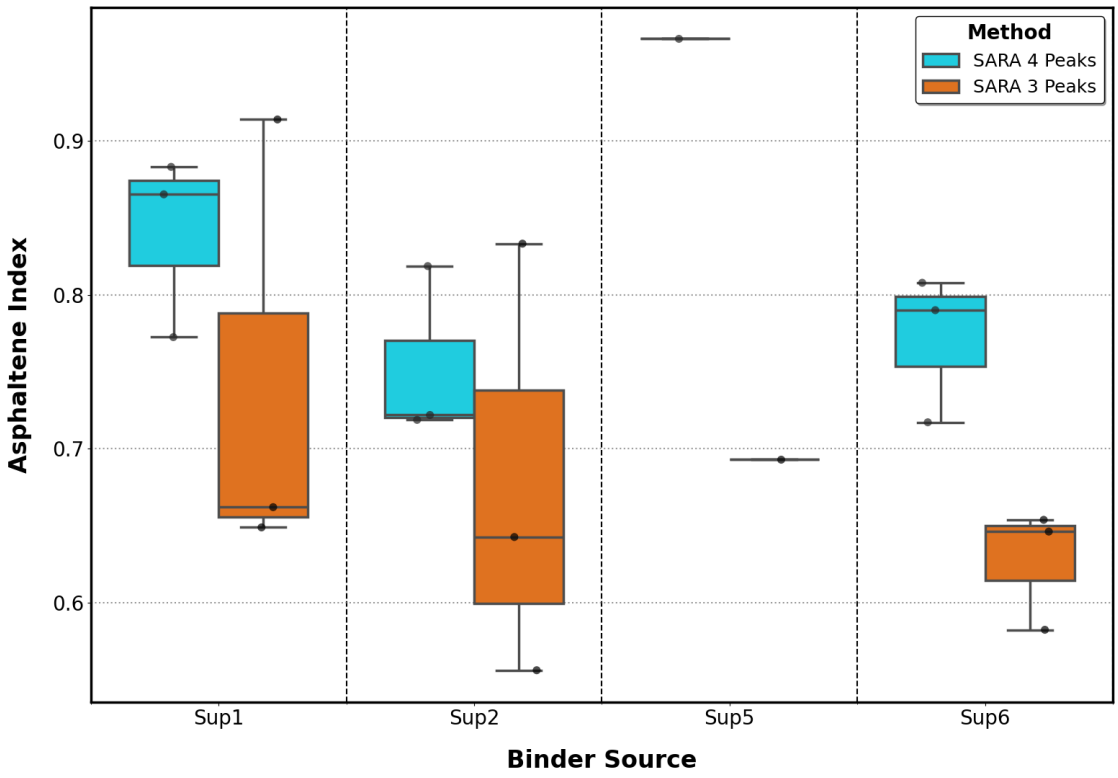


Figure 20 illustrates the variation of GPC fractions for PG 76-22 from different sources.

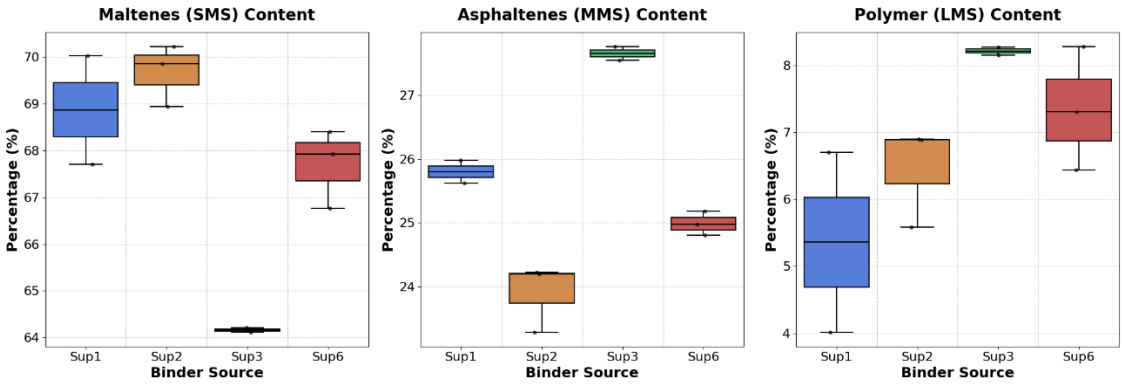
Maltenes (SMS—Small Molecular Size): For the PG 76-22 asphalt binders, the Sup2 source was the lightest binder, exhibiting the highest SMS content (≈69.7%). Conversely, Sup3 appeared as the heaviest source with the lowest SMS fraction (64.2%). It is important to acknowledge, however, that the differences in SMS content among the Sup2, Sup6, and Sup1 sources were relatively small, ranging from approximately 68 to 70%. This lack of practically significant difference suggested that, with the exception of the Sup3 outlier, the base solvent phases of these binders were chemically quite similar. The high maltene content in Sup2 suggested a system with greater relaxation capabilities, potentially aiding in fatigue performance, whereas the significantly lower maltene content in Sup3 indicated a stiffer, more rut-resistant matrix [7] [8] [9].

Asphaltenes (MMS—Medium Molecular Size): Sup3 led with the highest average MMS content (≈27.7%), followed by Sup1 (≈25.8%). Sup6 tracked closely with Sup1, with a start equation almost equal to 25.0%, and the overlap between the Sup6 and Sup1 distributions suggested that the difference in their asphaltene/MMS bodies start equation was not practically significant. Sup2 displayed the distinct lowest MMS content (≈23.9%). This

chemical profile confirmed that Sup3 was a heavy/structured binder, deriving its stiffness from a robust natural asphaltene network in addition to polymer modification. In contrast, Sup2 was chemically lighter, relying less on its natural asphaltene body to build structure [7] [8] [11] [12] [13] [17].

Polymer (LMS—Large Molecular Size): Sup3 exhibited the highest average polymer content (≈8.2%), closely followed by Sup6 (≈7.3%). While Sup2 showed a wide distribution (≈6.5%), Sup1 consistently showed the lowest polymer content (≈5.4%). Despite being the lowest in this group, Sup1's polymer content remained significantly higher than typical unmodified or PG 70 grades. The substantial polymer load in Sup3 and Sup6 suggested that these binders relied heavily on the elastomeric network for high-temperature rutting resistance. Sup1, with a comparatively lower polymer fraction, likely depended more on the synergy between its modification and its naturally stiffer asphaltene structure identified in the MMS analysis to achieve the PG 76 grade [11] [15] [17].

Figure 20. SARA components for PG 70-22 asphalt binders



The GPC test proved highly capable of distinguishing between the PG 76-22 binders from different sources, particularly in highlighting formulation strategies. While the base binder chemistry (SMS/MMS) for sources like Sup2, Sup6, and Sup1 showed overlaps with little practical difference, the polymer (LMS) content provided a clear differentiator. The test effectively distinguished between sources that relied on polymer dominance (Sup3: High LMS) versus those that utilized a balanced approach (Sup1: Moderate LMS, Moderate MMS). By quantifying these specific trade-offs, GPC offered a unique formulation fingerprint that can be complemented with rheological testing [7] [11] [16].

Figure 21 shows the saturate and aromatic component plots for the PG 76-22 asphalt binders.

Saturates: The Sup2 source consistently ranked highest, with a median saturate content of approximately 10.3% in the 4-peak method and 10.8% in the 3-peak method. This confirmed the paraffinic signature identified in other grades. In sharp contrast, Sup3 appeared as the distinct lowest saturate source (averaging ≈4.1% in 4-peak), indicating a highly aromatic or naphthenic crude origin. Sup1 and Sup6 fell into an intermediate range (approximately 6.5 to 7.5% in 4-peak), with overlapping distributions that suggested no practical significant difference between them regarding paraffin content.

From a performance standpoint, the high saturate content in Sup2 posed a potential risk for reduced adhesion (i.e., stripping) and physical hardening. Conversely, Sup3's low saturate fraction suggested better potential for adhesion and low-temperature stability, provided the asphalt balance was maintained. Both the 3-peak and 4-peak methods showed strong agreement in these rankings, validating that the saturate fraction is a robust chemical fingerprint easily isolated by n-heptane, regardless of the method used [11] [13] [14].

Aromatics: Sup6 exhibited the highest average aromatic content across both methods (≈48.7% in 4-peak; ≈52.5% in 3-peak), providing a strong solvent phase to disperse its polymer and asphaltene systems. Sup2 and Sup3 showed lower aromatic levels, ranging from 42 to 44% in the 4-peak method. Notably, in the 4-peak method, the box plots for Sup2 and Sup3 overlapped significantly, indicating that despite their vast differences in saturates, their resulting aromatic solvent phases were practically similar in quantity. The 3-peak method consistently yielded higher aromatic values (+3% to +6%) than the 4-peak method. For example, while Sup6 averaged ~48% in the 4-peak method, it spiked to over 52% in the 3-peak method. This systematic offset was likely due to the co-elution of light, semi-polar resins during the manual filtration step of the 3-peak method, which the 4-peak method successfully resolved into the resin fraction. While both techniques proved highly capable of differentiating binders based on saturate content (ranking: Sup2 > Sup6/Sup1 > Sup3), the 4-peak technique demonstrated superior capability for the aromatic fraction. By separating components in-situ on the rod, the 4-peak method avoided the false inflation of aromatics seen in the 3-peak method. It provided a more accurate assessment of the true solvent phase available to peptize the asphaltenes, revealing that Sup2 and Sup3 possessed similarly lean aromatic phases, a nuance partially obscured by the inflation in the 3-peak results [16] [17] [18].

Figure 21. 3-peak SARA component values for PG 76-22 from different sources

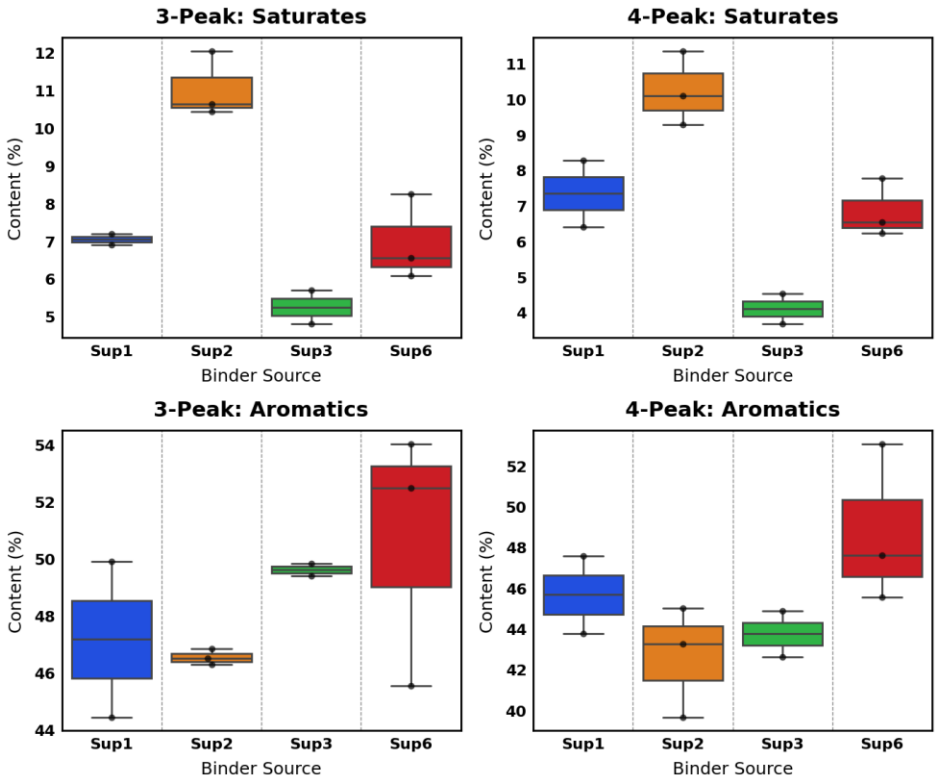


Figure 22 shows plots of SARA resin and asphaltene components for PG 76-22 asphalt binders.

Resins: The Sup3 source exhibited the highest resin content in the 4-peak method, averaging approximately 30.8%. When combined with its high asphaltene load, this observation confirmed Sup3 as a highly structured, well-peptized binder. However, this ranking was specific to the 4-peak method; in the 3-peak method, Sup3 displayed the distinct lowest resin values (≈21.4%), falling below both the Sup1 and Sup2 sources. Sup6 consistently showed the lowest resin content in the 4-peak method (≈24.2%), implying that it relied more heavily on its high aromaticity (i.e., solvency) rather than resins (i.e., peptization) for stability. Sup2 and Sup1 occupied the middle range in the 4-peak method; their distributions overlapped significantly, indicating that there was no practically significant difference between these two sources regarding resin peptization [11] [12] [13] [14].

The 4-peak method detected significantly higher resin content (+4% to +9%) than the 3-peak method. This was particularly important for these modified binders, as the 4-peak in-situ separation prevented the physical trapping of resins and polymers within the asphaltene

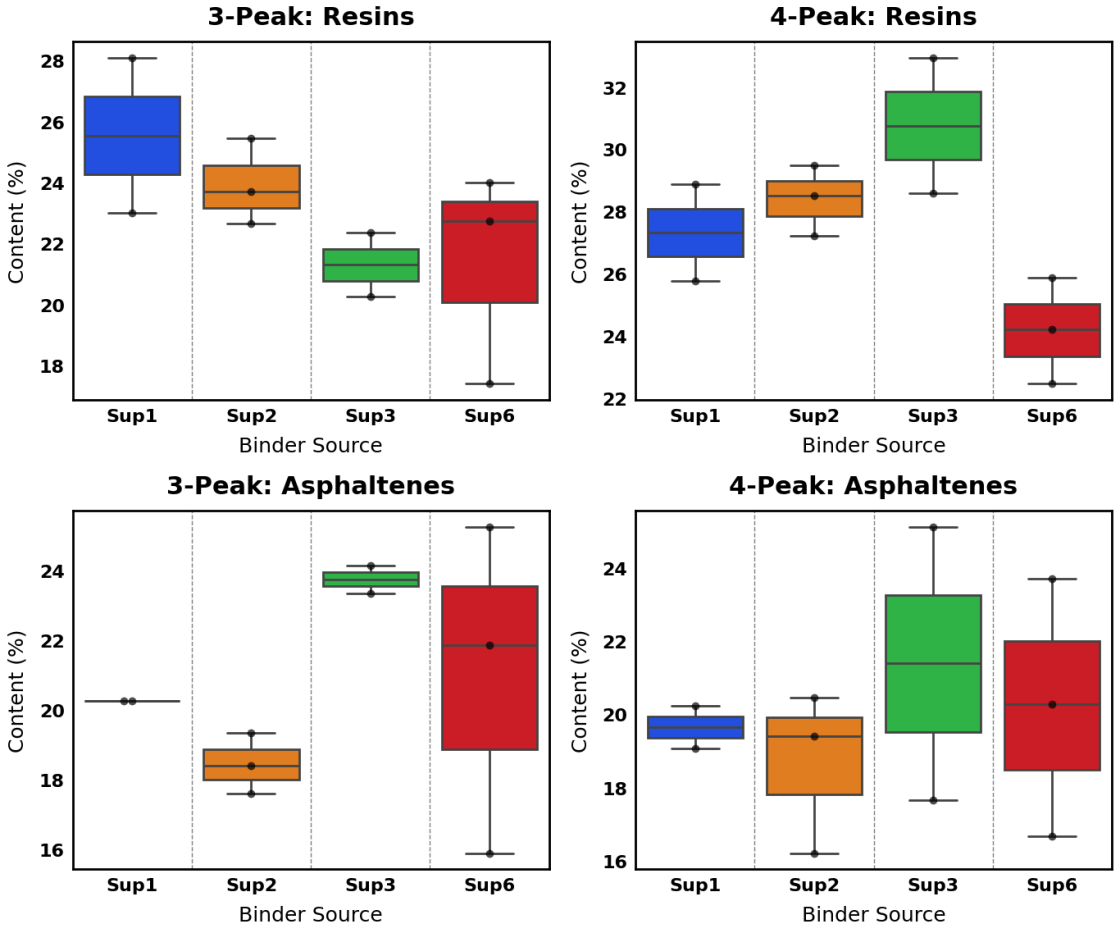
matrix, a phenomenon that likely reduced the apparent resin content in the 3-peak filtration method.

Asphaltenes: Consistent with the GPC analysis, Sup3 showed the highest average asphaltene content (≈21.4% in the 4-peak method). Conversely, Sup2 displayed the lowest asphaltene content (≈18.7%), confirming its chemically lighter nature. In the 4-peak method, Sup6 and Sup1 fell between these extremes with considerable overlap, suggesting their base asphaltene loads were practically similar. While there was generally good agreement between the techniques regarding the ranking (Sup3 > Sup6/Sup1 > Sup2), the 3-peak method yielded higher average values for the PG 76-22 modified Sup3 binder (≈23.8%). This inverse relationship with the resin results, where Sup3 3-peak resins were low, strongly suggested that the physical precipitation and filtration step in the 3-peak method captured some resinous and polymer-associated material as insoluble, effectively reclassifying them as asphaltenes [15] [16] [17] [18]. Generally, the Sup3 and Sup1 sources showed very tight distributions (low standard deviation), while the Sup6 source exhibited moderate variability in its aromatic and resin fractions, which was typical of the blending variations often seen in complex polymer-modified formulations.

The comparison of the SARA fractionation techniques showed that the 4-peak method was the most effective for differentiating binders based on resin content. By avoiding the physical filtration step, it provided a clearer distinction between peptized binders like Sup3 and solvated binders like Sup6. The 3-peak method tended to compress these differences or outright invert the rankings, as seen with Sup3, by losing resin fractions to the precipitated asphaltene phase.

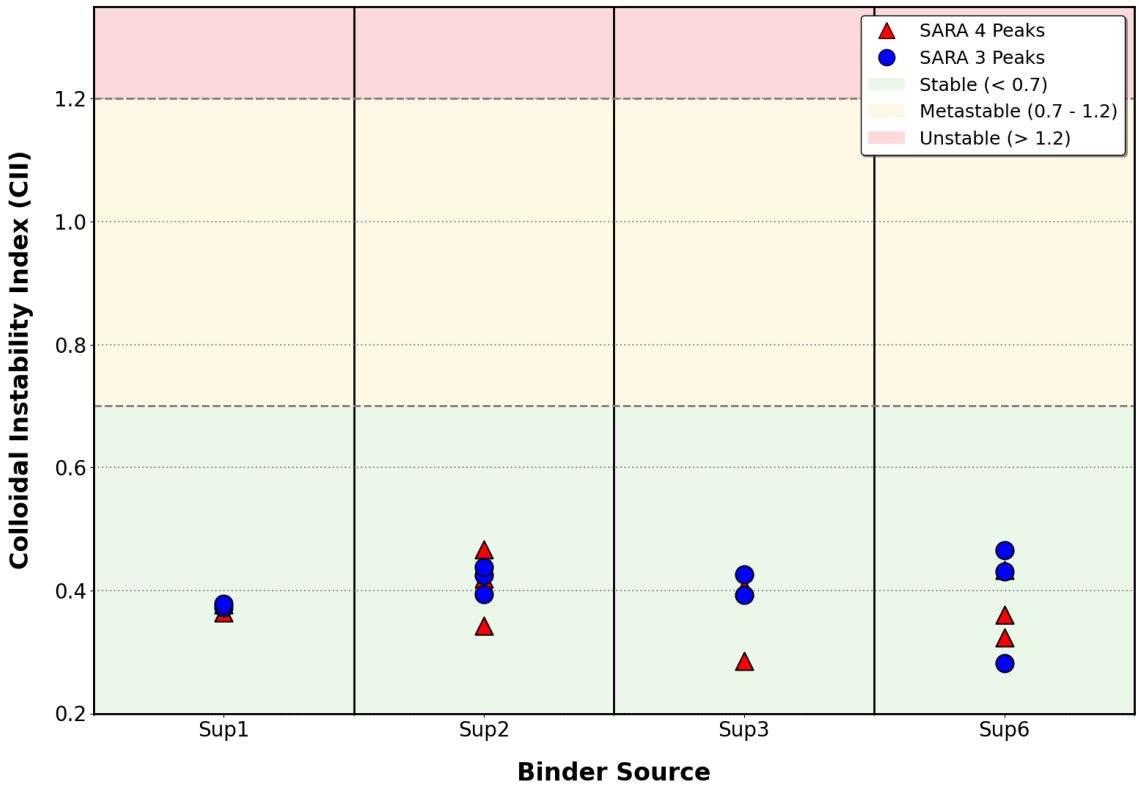
For asphaltenes, both methods distinguished heavy from light sources. However, the 3-peak method appeared more sensitive to interference from high polymer loadings, specifically in Sup3, which registered as pseudo-asphaltenes, whereas the 4-peak method provided a more conservative estimate that likely reflected the true asphaltene body [16] [17].

Figure 22. 4-peak SARA components values for PG 76-22 from different sources



Colloidal Instability Index: Figure 23 illustrates the Colloidal Instability Index (CII) values for the evaluated PG 76-22 binders. Notably, every source fell well within the stable (sol-type) zone (CII < 0.7), as highlighted by the green band. This confirms that the heavy polymer modification required for this grade did not compromise colloidal stability; rather, the aromatic and resin phases remained sufficient to effectively disperse the asphaltenes. When comparing sources, no practically significant differences were observed. Despite the distinct chemical profiles identified earlier, such as the high-saturate nature of Sup2 versus the high-resin content in Hu, every binder maintained a robust, stable structure. This uniformity demonstrates that, regardless of the formulation strategy, the solvent phases were successfully balanced to ensure effective peptization. Consequently, all sources appear chemically equivalent regarding their resistance to phase separation and gelations [14] [19] [21] [22].

Figure 23. CII values for PG 76-22 asphalt binders



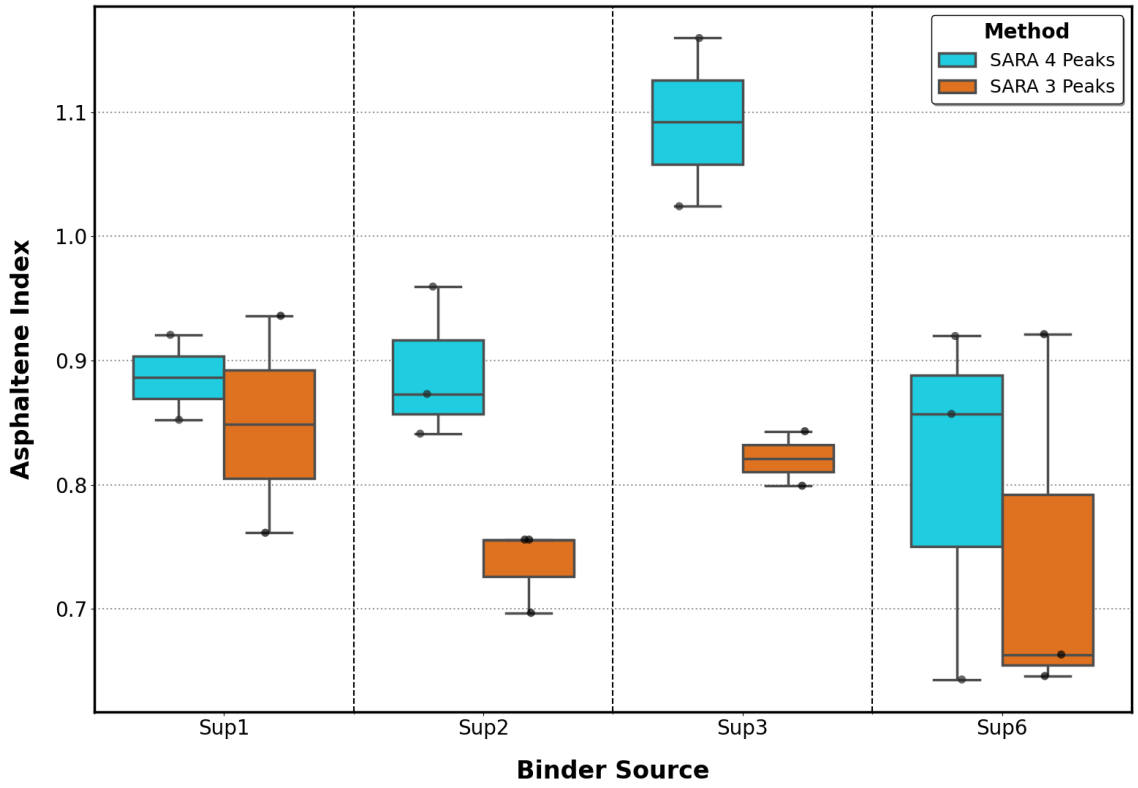
Asphaltene Index (AI): Figure 24 presents box plots for AI values for PG 76-22 binders from various sources. The Sup3 source exhibited the highest average AI in the 4-peak method (≈1.09), which was significantly higher than all other sources. However, in the 3-peak method, it dropped notably to 0.82. This large discrepancy suggested that the asphaltenes defined by the 4-peak method for the Sup3 source included a substantial fraction of highly polar material, likely heavy resins or polymer-associated complexes, that were soluble in n-heptane and thus filtered out in the 3-peak method. This indicated that Sup3 was chemically distinct, possessing a very high concentration of borderline polar molecules that contributed to its high stiffness. Similar to the Sup3 source, the Sup2 source also exhibited a substantial drop in AI in the 3-peak method compared to the 4-peak method.

Sup1 consistently showed AI values that were relatively similar across both methods (4-peak: 0.89; 3-peak: 0.85). The close agreement between methods suggested Sup1 possessed a well-defined asphaltene fraction that was chemically consistent, insoluble in n-heptane and immobile on the chromarod [15] [16] [17].

Higher AI generally correlates with increased stiffness and elastic recovery, which are essential for the high-temperature rutting resistance required of a PG 76 binder. However, if

the AI exceeds 1.0, as Sup3 did in the 4-peak method, the binder risks becoming overly structured. While excellent for rutting resistance, this could theoretically lead to brittleness at lower temperatures if the peptizing resin phase is compromised by aging. Sup6, with the lowest AI values, likely relied more heavily on its polymer modification (LMS) rather than its natural chemical structure to achieve the PG 76 grade. This configuration might allow for better initial flexibility, but could result in a faster loss of performance if the polymer degrades [14] [21] [22].

Figure 24. AI plots for PG 76-22 asphalt binders



Capabilities of GPC and SARA for Fingerprinting

The following section evaluates the capability of chemical characterization techniques to "fingerprint" different binder grades derived from the same source (Sup1, Sup2, Sup3, Sup5, Sup4, and Sup6). The primary goal of fingerprinting is to reliably distinguish between binder grades—for example, separating a PG 76 from a PG 67—solely on the basis of chemical composition data. Among the techniques evaluated, Gel Permeation Chromatography (GPC) offered an effective and robust means for distinguishing polymer-modified asphalt binders from unmodified binders. Because PG 70-22M and PG 76-22M binders are typically

modified with large molecular weight elastomeric polymers, GPC is exceptionally capable of detecting these additions via the Large Molecular Size (LMS) fraction.

Figure 25 presents the GPC polymer fraction (LMS) plots for various binder grades across different sources. The Sup6 source demonstrates the most distinct, non-overlapping stratification between grades. The unmodified PG 58 binders (blue circles) reside at the bottom with the lowest LMS content, followed by PG 67 (green squares). A clear jump is observed for the modified grades, with PG 70 (orange diamonds) in the middle and PG 76 (red triangles) at the top. This confirms a clear trend of increasing polymer content corresponding to increasing binder grade. Similarly, the Sup1 and Sup2 sources exhibited strong separation between the unmodified (PG 67) and modified (PG 70 and PG 76) binders. However, the distinction between the two modified grades for these sources was less pronounced than in Sup6, with a slight overlap observed between the polymer fractions of the PG 70 and PG 76 binders.

Figure 25. GPC polymer fractions for different binder grades

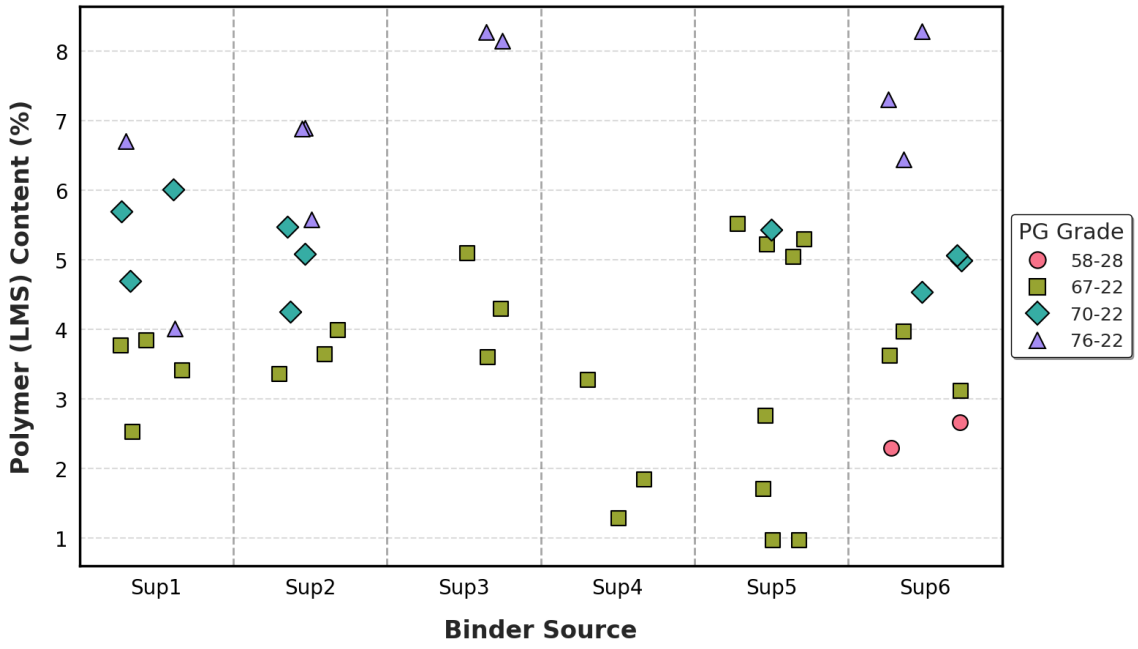
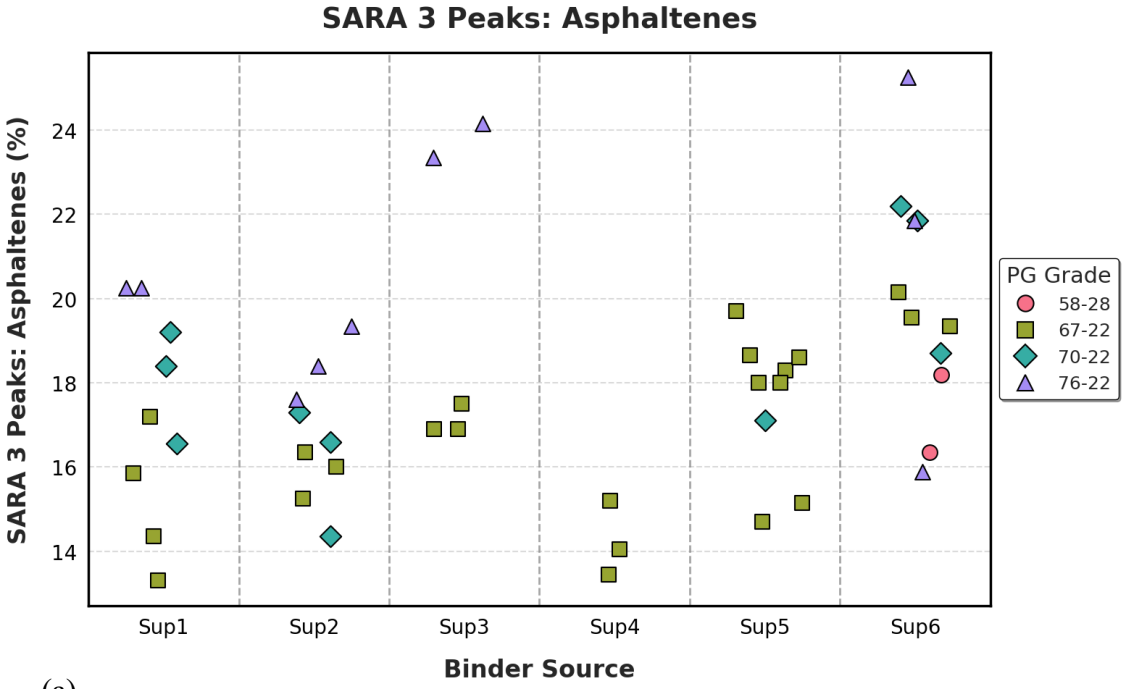


Figure 26 presents the SARA 3- and 4-peak asphaltene components for different binder grades evaluated in the study. Both SARA methods demonstrated moderate ability to distinguish different binder grades from the same source. The SARA methods separate binder components based on polarity/solubility. While heavier/stiffer grades often contain more asphaltenes, this is not a strict rule, which makes both the 3-peak and 4-peak methods poor

tools for fingerprinting different binder grades. For example, in the SARA 3-peak asphaltenes plot, the Sup6 PG 76-22M samples show massive variability, ranging from ≈16% to 25% and completely overlapping with the PG 67 and PG 58 grades. Additionally, for the SARA 4-peak asphaltenes plot for Sup6, the PG 58 (blue dots) has higher asphaltenes (≈20%) than some PG 70 samples (≈17%). This contradicts the expectation that stiffer binder corresponds to more asphaltenes.

Figure 26. SARA asphaltene contents for (a) 3-peak and (b) 4-peak methods



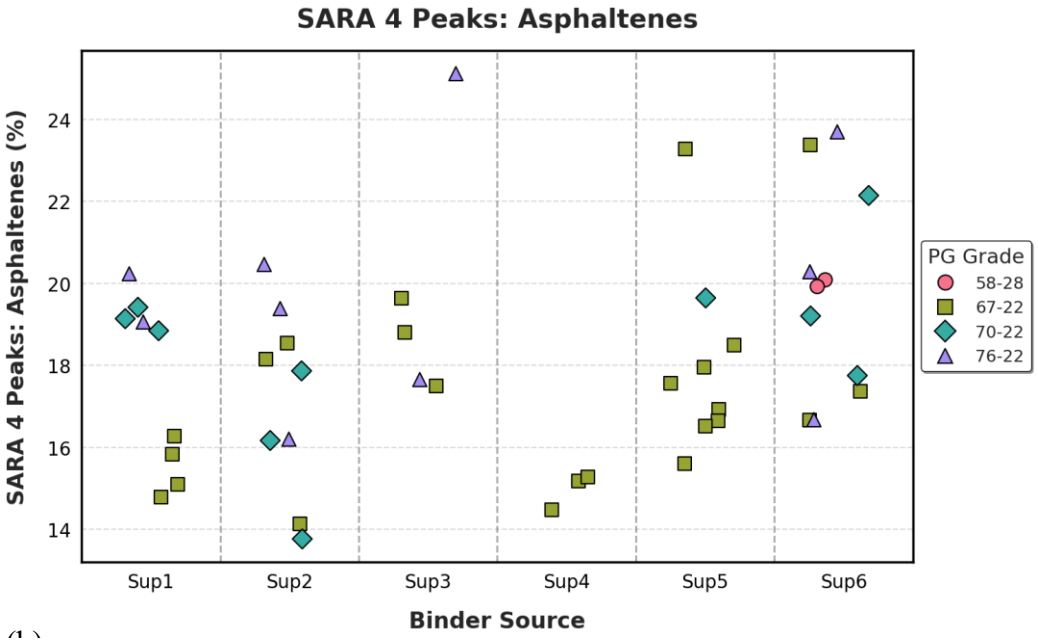
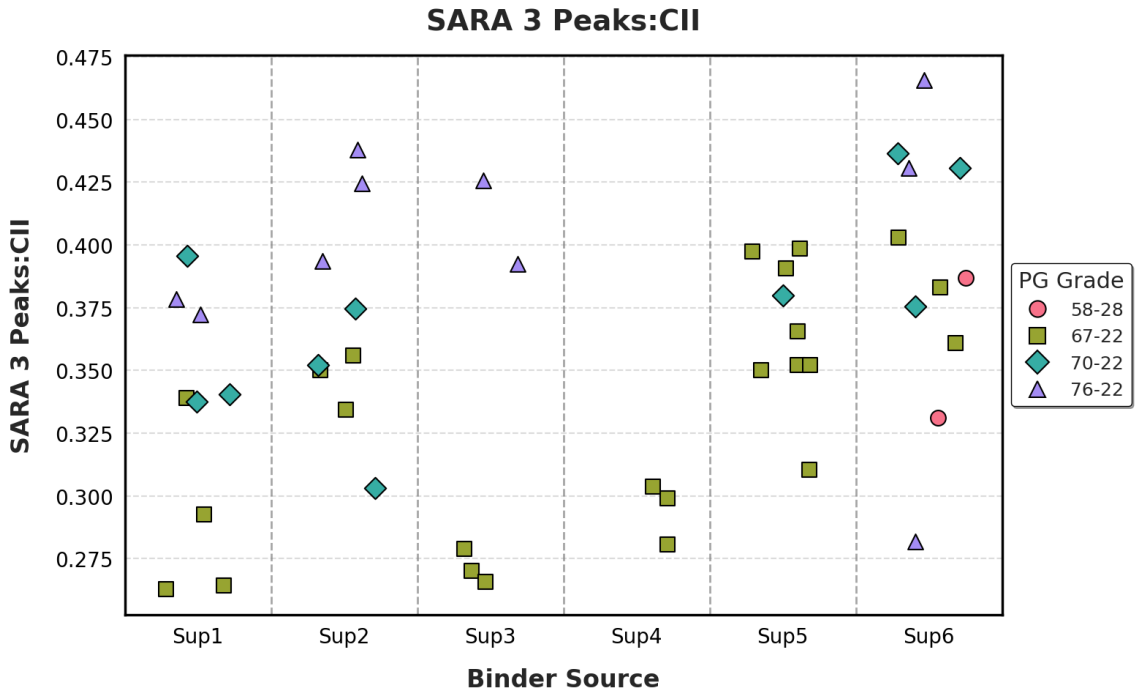
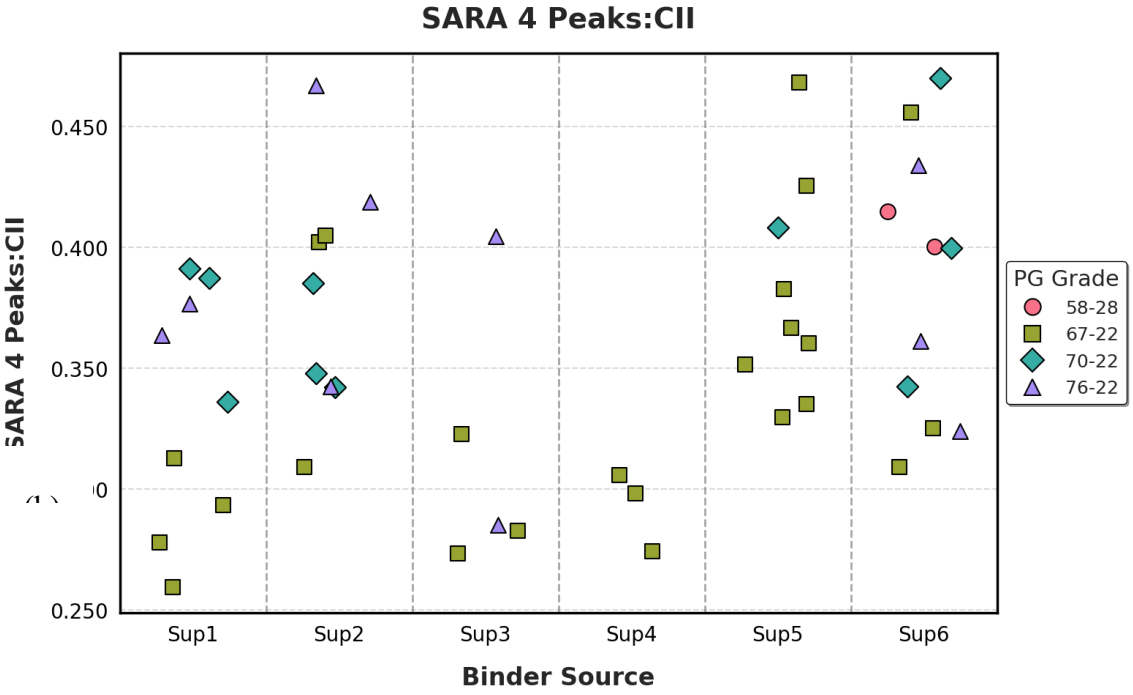


Figure 27 shows the CII values obtained from the SARA 3-peak and 4-peak fractionation techniques. Similar to the asphaltene contents, the CII, whether calculated from the 3-peak or 4-peak, remains inconsistent for fingerprinting different asphalt binder grades from the same source, as the ratios of aromatics and resins vary independently of the polymer modification.

Figure 27. CII values for (a) 3-peak and (b) 4-peak SARA fractionation




SARA 4 Peaks:CII
0.450
0.400
0.350
0.250
SARA 4 Peaks:CII
Sup1
Sup2
Sup3
Sup4
Sup5
Sup6
Binder Source
PG Grade
58-28
67-22
70-22
76-22

Conclusions

This study evaluated the capabilities of Gel Permeation Chromatography (GPC) and SARA fractionation for detecting changes in the chemical composition of asphalt binders. Analysis of 46 asphalt binder samples revealed significant differences between GPC and SARA fractionation results, with limited correlation between the two methods. These discrepancies are primarily due to the different focuses of the methods: GPC emphasizes the asphaltene fraction based on molecular weight, while SARA methods characterize binder components based on their solubility in specified solvents. The results also showed that GPC tends to classify certain portions of maltenes as asphaltenes based on molecular size, resulting in a significantly higher reported asphaltene content than SARA methods. Further, a comparison between the two SARA grouping methods, the 3-peak and 4-peak approaches, revealed notable differences. These stem from the higher level of separation achieved in the 3-peak method compared to the 4-peak method.

Based on these findings, GPC is valuable for analyzing larger molecular components, such as asphaltenes and polymer additives, whereas SARA methods are better suited for evaluating smaller molecular fractions, such as maltenes. Although both SARA methods demonstrated reasonably comparable performance, the 4-peak method, due to its elimination of pre-separation steps, was found to be more convenient for practical applications. Specific observations from the study are outlined below:

Chemical Characterization and Source Fingerprinting

Comparative analysis of PG 67-22, PG 70-22M, and PG 76-22M binders confirmed that GPC and SARA fractionation serve distinct, complementary roles. GPC proved most robust for identifying binder grade and modification levels. By isolating the Large Molecular Size (LMS) fraction, GPC effectively stratified binders by polymer content, showing a clear progression from unmodified PG 67 (< 4.5% LMS) to PG 76 (> 8% LMS). Conversely, SARA fractionation provided a chemical fingerprint of the base binder source, independent of modification:

- Sup2 Source: A high-saturate (~10%), paraffinic source with potential for physical hardening and reduced adhesion.
- Sup6 Source: A high-aromatic, solvated system (saturates < 8%) relying on solvency rather than resinous peptization to disperse polymers.

- Sup3 Source: A chemically heavy, structured binder with the highest asphaltene and resin contents (4-peak), indicating strong peptization and rutting resistance.
- Sup5 Source: Defined by a high resin load (~30% in 4-peak), acting as a robust sol-type binder with high colloidal stability.

Colloidal Stability

Despite chemical diversity, ranging from paraffinic Sup2 to asphaltene-rich Sup3, the Colloidal Instability Index (CII) confirmed all evaluated binders remained stable (sol-type, CII < 0.7). This uniformity demonstrates that formulation strategies for all binders, including the polymer-modified binders, successfully balanced solvent phases (i.e., aromatics and resins) to ensure effective asphaltene peptization, regardless of crude source.

SARA Fractionation: 3-Peak vs. 4-Peak Methods

A critical divergence exists between SARA fractionation methods. The 3-peak method, which relies on manual filtration, consistently overestimates aromatics and underestimates resins due to light resin co-elution and physical entrapment within the polymer-asphaltene matrix. In contrast, the 4-peak method utilizes in-situ separation to offer superior resolution for modified binders, allowing for the accurate classification of high-polarity fractions. However, the 4-peak method faces specific limitations when applied to high-polarity binders. These include: (1) the retention of polar components at the origin; (2) heteroatom interference with quantification; and (3) sensitivity to sample spot size. While previous research has indicated that these factors can lead to a lack of reproducibility and inconsistent results, other studies argue that historical skepticism regarding TLC-FID stems largely from manual spotting errors and older detector designs [18] [19] [23]. To enhance the reproducibility of the 4-peak method, modern protocols recommend the use of automated spotting devices and the doping of chromarods with Copper (II) Sulfate solution. Further, optimizing spot size is critical; research indicates that while small spot sizes (1 to 1.5 mm) cause resins to smear into asphaltene peaks, larger spot sizes (3.5 to 4 mm) improve resolution, allowing for the accurate deconvolution of polar content into distinct resin and asphaltene peaks [18] [23].

Recommendations

Based on these findings, GPC is valuable for analyzing larger molecular components, such as asphaltenes and polymer additives, while SARA methods are better suited for evaluating smaller molecular fractions, such as maltenes. Although both SARA methods demonstrated reasonably comparable performance, the 4-peak method, due to its elimination of pre-separation steps, was found to be more convenient for practical applications.

Acronyms, Abbreviations, and Symbols

Term	Description
AASHTO	American Association of State Highway and Transportation Officials
BHT	Butylated hydroxytoluene
CII	Colloidal Instability Index
DOTD	Louisiana Department of Transportation and Development
FHWA	Federal Highway Administration
ft.	foot (feet)
GPC	Gel Permeation Chromatography
in.	inch(es)
lb.	pound(s)
LMS	Large Molecular Size
LTRC	Louisiana Transportation Research Center
MMS	Medium Molecular Size
PG	Performance Grade
SARA	Saturates, Aromatics, Resins, Asphaltenes
SMS	Small Molecular Size
THF	Tetrahydrofuran
TLC-FID	Thin-Layer Chromatography with Flame-Ionization Detection

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