OPEN ACCESS
ECOCYCLES
ISSN 2416-2140
Scientific journal of the
European Ecocycles Society

Ecocycles, Vol. 10, No. 1, pp. 68-83 (2024)
DOI: 10.19040/ecocycles.v10i1.413

RESEARCH ARTICLE

Optimizing bio-bitumen mixes through response surface methodology

Penki Ramu [*1,2] **Subrat Kumar Rout** [3] **Aditya Kumar Das** [4]
[*1]*Assistant Professor of Civil Engineering, GMR Institute of Technology, Rajam, Vizianagaram, A.P, India*
[2]*Ph.D. Scholar, Dept. of Civil Engineering, ITER, Siksha 'O' Anusandhan Deemed to be University, Bhubaneswar, India*
[3]*Professor, Civil Engineering Department, Siksha 'O' Anusandhan Deemed to be University, ITER, Bhubaneswar, India*
[4]*Assistant Professor, Department of Civil Engineering, National Institute of Technology, Rourkela, Odisha, India*

Corresponding author: Penki Ramu. email: ramu.p@gmrit.edu.in

Abstract –Bio-bitumen, a sustainable alternative to petroleum-based bitumen, is gaining popularity owing to its environmental advantages and potential to address depleting crude oil sources. The purpose of this study is to use Response Surface Methodology (RSM) to optimize bio-bitumen characteristics for sustainable pavements. Bio-bitumen is produced by combining conventional bitumen with biochar, cashew nutshell liquid, waste engine oil, and phthalic anhydride. This study uses RSM to investigate how these components (biochar, cashew nutshell liquid, waste engine oil, and phthalic anhydride) influence important bio-bitumen properties (penetration, ductility, softening point, and elastic recovery). A 2^4 factorial design with 27 trials was employed to optimize the mixing procedure. Statistical analysis, employing visualizations like contour plots and surface plots revealed an optimum bio-bitumen combination having 15% biochar, 1.71% cashew nutshell liquid, 0% waste engine oil, and a phthalic anhydride concentration ranging from 4.54% to 7.5%. This study illustrates the efficacy of RSM in optimizing bio-bitumen for sustainable pavements, paving the way for more environmentally friendly road construction.

Keywords – Response Surface Methodology, Biochar, CNSL, Waste engine oil, Phthalic anhydride.

Received: March 15, 2024 Accepted: April 5, 2024

1. INTRODUCTION

A radical transition towards sustainable practices is currently taking place in the worldwide construction sector, which is the backbone of contemporary infrastructure (Fei et al., 2021). The importance of bitumen, a vital component of asphalt materials, is highlighted in this paradigm. Bitumen is a linchpin in the area of building and road infrastructure due to its adaptability, adhesive capabilities, and longevity (Kamoto et al., 2020) (Polo-Mendoza et al., 2023) (Polacco et al., 2006). Not only that, but it also fulfilled its function as a pavement binder, sealant, preservative, and noise barrier (Anupam et al., 2023). However, as the world gets closer to a sustainable future, worries about how traditional bitumen compositions affect the environment have emerged (Anupam et al., 2023; Mohd Hasan et al., 2019). The building industry will become more robust and ecologically conscientious as a result of the urgent need to research and use bio-based alternatives (Ahmed Ali et al., 2020; Maraveas, 2020). The goal of this research is to optimize the formulation of bio-bitumen to address pressing issues related to sustainable construction and building materials.

The information reveals that bitumen, a mixture of natural gas and crude oil, is created by the transformation of biological matter. It also examines how human ingenuity and the forces of nature have combined to create modern constructed environments (Sanei, 2020). Bitumen reserves may be found in many forms all around the world, which helps with a variety of uses. Lake bitumen, which is extracted from lakes and reservoirs, is utilized for industrial and road-building purposes. Sedimentary rock formations include rock bitumen, sometimes referred to as oil sand, which is utilized to make bitumen-based industrial goods and synthetic crude oil (Anupam et al., 2023). A natural alternative to asphalt, gilsonite is a hydrocarbon substance that may be ground into a powder (Kim, 2014). Sand, clay, water, and bitumen are combined to create bituminous sand, which is present in sedimentary rock formations and provides improved stiffness, durability, and resistance to rutting in paving operations (Anupam et al., 2023).

According to Chalailleux et al. (2021) and Porto et al. (2022), the most often used binder in road pavements is petroleum bitumen, which is produced by fractional distillation. Through oxidation, residual bitumen undergoes treatment and changes that improve its hardness and viscosity. Various penetration grades are produced for road construction using this procedure. Direct processing involves forcing air through a heated residue; alternatively, it can be combined with petroleum distillates or mixed mechanically. Preparing various grades—which might range significantly in hardness and penetration values—requires oxidation. Oxidization efficiency is highly dependent on the type of residual bitumen that is employed. Aging, elasticity loss, and inadequate adherence to stone substrates are all problems associated with residual bitumen (Working Group on Assessment of Carcinogenic Risk to Humans, IARC, 2013).

Road builders must improve the quality of bitumen by adding surfactants and polymer materials (Caputo et al., 2020). The production of residual bitumen is cumbersome, time-consuming, and complex, and its thermal susceptibility is a serious problem. The price of bitumen is strongly related to crude oil prices, leading to increased costs (Ingrassia et al., 2019). Bitumen deposits are shallow, vertically placed 0–500m above Earth's surface, with natural conditions above. They are used for drinking and economic purposes. However, pollution of underground water is a major concern, with heavy oils and bituminous deposits containing dissolved hydrogen sulfide, aluminum, and bromine. Violations during sustainable development can destroy column integrity and contaminate upper freshwater (Larter & Head, 2014). Bitumen exposure can lead to lung and stomach cancer, bronchitis, and emphysema, as well as damage to the liver, kidneys, and nervous system. The main hazard is the high temperature used for construction, which can release hydrogen sulfide gas into the air, causing suffocation and even death. Asphalt fumes, which are vaporized, can pollute water, water, and soil, affecting both humans and the environment. Workers exposed to bitumen fumes are more affected, with olfactory paralysis, respiratory distress, and fatalities occurring if the air volume exceeds 100 ppm (Mary, 2010).

The asphalt industry uses elastomeric polymers to reduce heat susceptibility and deformation, resulting in polymer-modified bitumen (PMB). However, PMBs are expensive, have low aging resistance, and poor storage stability. PMB combines bitumen and polymers for superior mechanical properties, enhancing elasticity, strength, cohesion, and fatigue resistance. Its impressive temperature stability makes it indispensable for applications like road pavements and protective coatings, despite its drawbacks (Emtiaz et al., 2023; Zhu et al., 2014). On the other side, the dark hue of a substance contributes to the heat island effect, contributing to the greenhouse effect, global warming, and climate change (Ibrahim et al., 2018). Natural bitumen was once the primary source of bitumen for pavement construction before the oil boom era. However, as vehicular traffic density and loads increased, petroleum production increased, leading to petroleum-sourced bitumen being used instead. The natural bitumen reserve is estimated to be around 1,856,853 billion barrels. As oil resources are predicted to deplete within 30 years, less bitumen is available for engineering applications. The reserve life is anticipated to be 46 years with an annual global demand of roughly 100 million metric tons (Gürer et al., 2020).

Apart from the negative impacts of bitumen manufacturing and its use as a construction material, waste materials generated from various sources also harm human health and the environment (Siddiqua et al., 2022). Examples linked to the same are discussed below. Due to its high lignin content, black liquor (BL), a waste liquid from papermaking, is a major source of water contamination. Although lignin is the only naturally aromatic recyclable material, its effective utilization rate is less than 3% (Tao et al., 2023). Waste cooking oils in open landfills cause soil and water pollution. Waste oil recycling is introduced to address high building costs and waste disposal issues (De Feo et al., 2023). Solid biomass waste, produced in large quantities, is ineffectively managed due to its low commercial value (Saleem, 2022).

According to the International Road Federation, the transportation sector accounts for more than 20% of energy-related carbon dioxide (CO2) emissions and over 15% of global greenhouse gas emissions (He et al., 2023). Methane emissions are responsible for 25% of global warming, and some of the main sources of methane include the manufacture of fossil fuels and the burning of biomass (Sri Shalini et al., 2021). The COP 21 Paris Agreement, a global referendum, aims to reduce CO2 emissions and reduce global temperature to below 2°C. Countries like the Netherlands have committed to a 95% reduction in emissions by 2050, driven by a shift from cars to bicycles, public transport, and electric vehicles. However, these regulations could result in a decline in the market for petroleum products, which would hurt bitumen-dependent sectors like the transportation sector (Chen et al., 2023). Relevant businesses are likewise concerned about the depletion of crude oil resources. According to MIT researchers and the Concrete Sustainability Hub, carbon capture and neutralization techniques can make pavement mix carbon-neutral by 2050. In the near run, this can lower greenhouse gas emissions; but, to minimize the impact of carbon on new roadways, creative solutions and careful material selection are required (Sizirici et al., 2021).

The depletion of crude oil reserves, refinery advancements, and rising demand for highway infrastructure are some of the reasons driving up the need for alternative bitumen in pavement building globally (Adebiyi & Akhigbe, 2015). Researchers are investigating environmentally friendly substitutes made from renewable biomass sources, such as bio-bitumen. By lowering dependency on fossil fuels and mitigating their environmental effects, these organic substitutes can help create a more environmentally friendly future (Sher et al., 2022). The road sector has to employ renewable resources like garbage or byproducts to lessen its carbon footprint and dependency on petroleum-based goods (Ingrassia et al., 2019). To address problems, the circular economy and sustainability strategy can encourage community, business, and academic research.

According to (Penki & Rout 2023) sustainability is the process of protecting natural resources for future generations without sacrificing the requirements of the present. Recycled materials may be successfully used and energy consumption reduced to improve the sustainability of pavement (Yaro et al., 2023). A circular economy slows and closes material and energy cycles, reducing waste and use of resources. Pavement industries can make use of a 4R regenerative system, which stands for recycling, repair, return, and reuse (Kirchherr et al., 2023).

Carbon-rich biomass is commonly utilized for producing biochar, a pyrogenous, organic material derived from the pyrolysis of various plant or animal waste, which lowers building and maintenance costs while enhancing pavement strength and longevity. There are major social and economic advantages to this strategy (Zhang et al., 2022). Pavement engineering can employ bio-based binders, which are made from renewable resources including vegetable oils, lignin, and charcoal, to lower greenhouse gas emissions, boost the circular economy, and increase pavement performance. Depending on their source, processing technique, and intended use, they can be utilized in a variety of ways, such as bio-asphalt, bio-concrete, and bio-composite. These substances can lessen their negative effects on the environment while simultaneously enhancing the concrete's strength, resilience, and self-healing qualities (Su et al., 2018; Weir et al., 2022). Research is being done in the bitumen business to enhance its qualities, especially in road paving procedures. Although traditional additives have been employed, workers are at risk due to their strong chemical nature and harmful emissions. As appropriate bitumen additives, researchers are currently looking into biomaterials such as bio-oils, gum, polysaccharides, natural waxes, and natural rubber. The goal of this approach is to create industrial processes that are more durable, affordable, and safe (Abe et al., 2022).

Although they provide potential advantages, bio-based binders for pavement engineering come with drawbacks. They need to be evaluated for environmental effects, economically feasible, and technically feasible. Waste cooking oil can improve fatigue resistance, but it softens bitumen. Bio-oil generated from palm kernel oil can be used to address moisture damage resistance. Although bio-oils have a higher oxygen content, viscosity, and density, they can become unstable during storage. Producing bio-oil capsules and mixing them with bituminous concrete can result in self-healing. Bio-oil-modified asphalt binders improve low-temperature crack and fatigue resistance but may decrease high-temperature stability and moisture resistance. Biochar (BC) increases asphalt binder performance in high-temperature climates but reduces performance at low temperatures.

Through response surface methodology-based design of experiments, scientists may determine the best bio-bitumen formulation that strikes a compromise between cost and performance. Researchers may systematically alter the composition and properties of bio-bitumen and assess how these changes affect important performance attributes including viscosity, elasticity, and adhesion by using response surface technique-based design of experiments. Using this approach, one may determine the optimal combination of modifiers and bio-oil fractions to enhance the performance of bio-bitumen, such as hybrid bio-oils or crumb rubber. Furthermore, because bio-oils age during storage and increase high-molecular-weight fractions and adhesive characteristics, it is imperative to optimize the bio-oil content in the formulation to ensure the intended adhesive strength and performance of the bio-bitumen (Cai et al., 2021).

Response surface technology allows researchers to systematically change the quantities of modifiers and bio-oil in the bio-bitumen formulation. This helps them to figure out how much bio-oil and modifiers to add to maximize the adhesive strength, yield stress, stiffness, and elasticity of the bio-bitumen (Ameri et al., 2023). This optimization study offers important insights into the potential of a bio-based economy and the viability of using bio-bitumen as a viable substitute for traditional bitumen in a range of engineering applications. It also advances the development of sustainable and environmentally friendly materials for road construction. Additionally, carrying out durability evaluations, rheological analyses, and mechanical tests on the optimized bio-bitumen formulation will yield important details about its engineering potential and performance in practical applications. A thorough experimental program based on a design of trials based on the response surface approach will be carried out to accomplish this. By adjusting the ratios of bio-oil fractions and modifiers such as crumb rubber or hybrid bio-oils made from renewable resources, the goal is to optimize the formulation of bio-bitumen. These bio-binders' effects on an asphalt mixture's behavior will be assessed, with a focus on fatigue resistance, fracture resistance, permanent deformation, indirect tensile strength, and indirect tensile stiffness modulus (Gaudenzi et al., 2021).

1.1. Background

The purpose of utilizing phthalic anhydride in bio-bitumen is to react with bio-oil to improve the hydrophobicity and moisture damage so, this is called a chemical modification of bio-oil (Zhou et al., 2020). WEO and WCO are significant environmental pollutants, potentially polluting rivers and natural resources. Proper disposal is crucial to prevent environmental and municipal issues. Unprocessed waste oil dumping in landfills or rivers can lead to severe ecological issues like eutrophication, disrupting marine life's oxygen supply (Li et al., 2019). Thermogravimetric analyses on coconut shell biomass revealed a weight loss of 95.08% at 699°C due to thermal decomposition. The decomposition process was divided into three stages, with the second stage accounting for 50.14% of mass change. The DSC (Differential scanning calorimetry) curve showed a peak at 477°C, aligning with the chosen pyrolysis temperature for biochar synthesis. The surface morphology of coconut shell biochar showed a rough surface with many voids, dominated by carbon and oxygen. The FTIR (Fourier Transform Infrared Spectroscopy) spectrum revealed strong bands at various locations for biochar's adsorption capabilities (Jegan et al., 2020).

The inclusion of OMT (organic montmorillonite) and WEO enhances the bitumen binder's effectiveness during fatigue and self-healing. Evaluation indicators including fatigue life recovery (FLR), modulus recovery (MR), and dissipated energy recovery (DER) were selected based on a fatigue-healing test to ascertain the bitumen's level of healing. When compared to the original bitumen, bitumen treated with 9% WEO exhibits a considerable improvement in FLR, MR, and DER, regardless of the OMT level. When compared to the original bitumen, the bitumen treated with 2% OMT and 3% WEO had rutting factors that were 18.6% better (Lu et al., 2023). Cashew nut shell liquid (CNSL) enhances bitumen-aggregate adhesion, resulting in improved stripping resistance and mechanical properties in asphalt compared to conventional asphalts, thereby preventing moisture damage (Joseph & C S, 2023).

After the literature was reviewed, a combination of 15% biochar (BC), 1.71% cashew nutshell liquid (CNSL), 0% waste engine oil (WEO), and 15% phthalic anhydride (PA) was suggested as a possible place to start for bitumen modification. Several laboratory tests were carried out utilizing a trial-and-error methodology to fine-tune these values and determine their respective contributions. At different concentrations, every substance (BC, CNSL, WEO, and PA) was independently assessed. Tests were conducted on biochar at 0, 5, 10, 15, and 20%; CNSL and WEO varied from 0 to 10%; and PA ranged from 0 to 20%. The optimization of each component's impact on the bitumen characteristics was made possible by this methodical examination.

1.2. Research Gap and Objective

Limited study has investigated the combined impacts of biochar, waste engine oil, cashew nutshell liquid, and phthalic anhydride on bio-bitumen performance utilising Response Surface Methodology (RSM) for optimisation. This work fills a gap by studying the effect of various additives (biochar, cashew nutshell liquid, waste engine oil, and phthalic anhydride) on critical bio-bitumen parameters (penetration, ductility, softening point, and elastic recovery) using RSM. Our goal in optimising the formulation using RSM is to determine the optimal combination of additives for producing high-performing and sustainable bio-bitumen mixes. Finding the best additive combination to create high-performing and sustainable bio-bitumen mixtures is the goal of formulation optimisation using RSM.

2. Response Surface Method

Even if they have their uses, traditional material analysis like trial & error techniques can be laborious when handling several variables for optimization. Here are some reasons why material optimization benefits greatly from response surface methodology (RSM): Valuable tool for material optimization due to its ability to handle multiple variables, reduce experiments, and develop mathematical models that predict material properties based on input variables. It uses the statistical design of experiments to efficiently capture the response surface, allowing for visualization and optimization of desired properties (Aydar, 2018; Kumari & Gupta, 2019).
Process efficiency requires optimization, and traditional methods often overlook interaction effects, increasing costs and time. Design-Expert software offers modeling, statistical analysis, and optimization for experimental design. It includes programs like surface response, full factorial, fractional factorial design, mixing, and D-optimal designs. RSM, a statistical approach for optimizing engineering design and operations, was created by Box and Wilson in 1951.

The Design of Experiments (DOE) approach can be used to investigate the impact of independent factors on experimental outcomes, optimizing test variables and obtaining optimal results. Statistical modeling techniques like RSM are crucial for determining correlations between independent variables. RSM is a method that uses input data to create equations, describe independent variables, and evaluate their impact. It improves laboratory test effectiveness by modeling and optimizing factors with fewer tests. RSM has improved asphaltic concrete mixes and asphalt binder performance, providing an empirical model for predicting peak performance and reducing failure rates. The box-Behnken design optimizes mixed parameters.

This research focuses on finding optimal proportions for bio-bitumen with the inclusion of biochar, CNSL, WEO, and PA in 60/70 grade virgin bitumen using RSM. In the Design of the Experiment application in Minitab software for optimization, the Response Surface Method is applied. The study combines experimental and analytical analysis to provide precise and accurate results for an optimized bio-bitumen composite. The research aims to contribute to sustainable construction solutions by optimizing bio-bitumen formulation. Despite growing interest, there is a critical gap in understanding and formulating these alternatives. This study addresses existing limitations in bio-bitumen knowledge, offering a comprehensive response to challenges posed by traditional formulations and aiming for more sustainability in future construction practices.

3. Materials and Testing

3.1. Ingredients and Composition

The study's binder, 60/70 dmm, came from the Visakhapatnam Tiki Tar Industries (Baroda) Ltd in India and complies with IS 73(2013) and IS 1203-1978. Table 1 shows the basic features of the stated binder. The Waste engine oil is brought from repair garages in Rajam, Andhra Pradesh, India. While waste engine oil is not strictly bio-based, it may be considered a sustainable asphalt alternative due to its reuse and waste reduction potential. In this study, WEO is pre-processed to eliminate contaminants before being used. This study's waste engine oil is an oily, black liquid that serves as a solvent. In this work, slow pyrolysis of coconut shells was utilized to create biochar, which was employed as a filler or modifier because of its unique properties like very uneven, porous and abrasive surface that promotes physio-chemical interactions with the bitumen binder. Table 2 displays this biochar's physical attributes. The phthalic anhydride was collected from the Labogens fine chem industry, Ludhiana, Punjab, India. Even though it isn't biobased, encourages sustainability by lowering the amount of virgin bitumen by reacting with biooil to increase its hydrophobicity and resistance to moisture damage. This might result in a pavement solution that is more resilient and long-lasting.

Table 1. Bitumen physical properties

Physical test	Result	Standard value	Specification	Test method
Penetration value	5.23mm	60-70 | 50-70	ASTM D5-13 | IS:73	IS 1203: 1978
Softening point	50	49-56 | >47	ASTM D36-14 | IS:73	IS 1205: 1978
Ductility value	>70	>100 | >40	ASTM D113-17 | IS:73	IS 1208: 1978

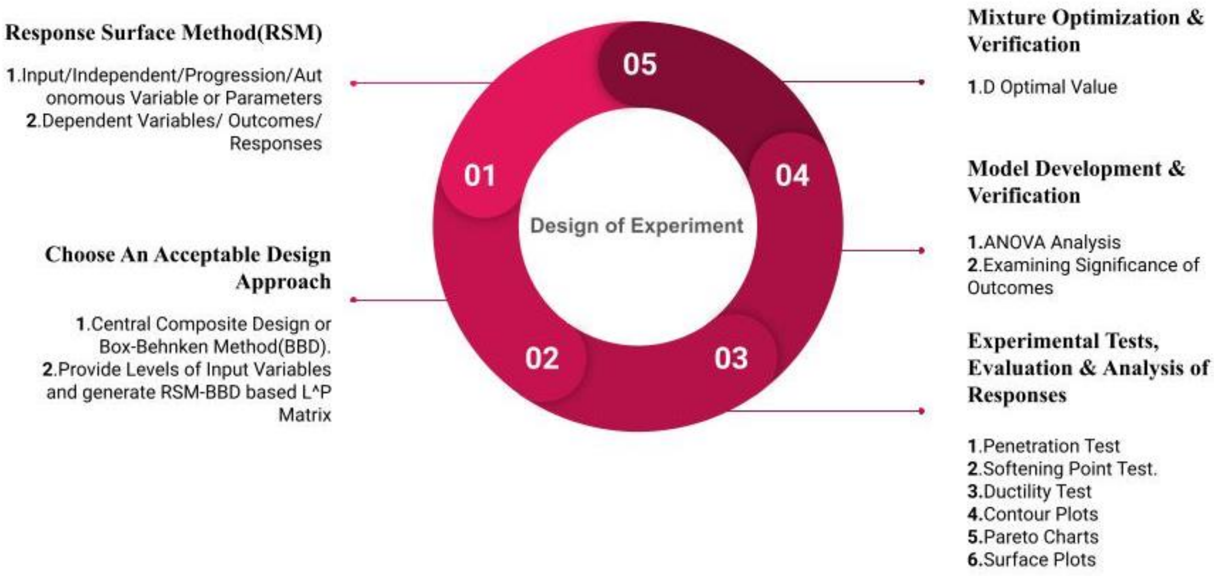

Figure 1. Road Map for Mixture Optimization using Response Surface Methodology

Table 2. Biochar characteristics

Test Name	Result
Rigden void (RV) content	35.48%
Methylene Blue (MB)	9ml
German filler (GF) test	35g
Bulk density	1.47g/cc
Hydrophilic coefficient	0.95
pH value	9.09
Electrical Conductivity	260 µS

3.2. Mixing Process

The mixes were prepared using low-shear mixing. Before mixing, the 60/70 penetration bitumen, bio-oils, and blend ingredients were heated individually to 160 °C for 30 minutes. Following a temperature-controlled hot plate, the bitumen was put on it and the oil was added once both the bitumen and oil had achieved 160 °C. For thirty minutes, at 300-600 RPM, the blending temperature was maintained at 160 °C. The moisture in the bio-oil and biochar was extracted by heating it to 100 °C for 60 minutes before blending, to avoid the bitumen blend from foaming (Tabaković et al., 2023).

4. METHODOLOGY

The current experimental program was designed using the response surface approach, which analyses the impact and interactions of multiple factors on a dependent variable. The experimental data were obtained from the performance properties of bio-bitumen. When there is no fit or overfitting resulting in the removal of irrelevant or extraneous components, the most acceptable transformation is chosen as the regression model. To create the final model, the linear regression assumptions must be met. To attain higher performance properties, the combined impact of Biochar, CNSL, WEO, and PA is optimized. Figure 1 demonstrates the exact procedures required to construct and optimize response models.

Table 3. The levels of variations in independent/ progression variables

Variable's	Minimum	Maximum
Biochar	0	15
Cashew Nut Shell Liquid (CNSL)	0	2
Waste Engine oil (WEO)	0	3
Phthalic anhydride (PA)	0	15

Factors and variable levels are required to be supplied in the DOE of RSM autonomous variables, as indicated in Table 3 for the four proposed responses. For the 27 mixtures listed in Table 4, the four-factor BBD approach is used to assess the impact of biochar, cashew nutshell liquid, waste engine oil, and phthalic anhydride on the performance properties of bio-bitumen.

Table 4. 27 trials with proportions of independent variables were recommended by the 24 matrices RSM-BBD

Std Order/ Run Order	Biochar	CNSL	WEO	PA	Penetration	Ductility	Softening point	Elastic Recovery
1	0	0	1.5	7.5	75	34.5	60	95%
2	15	0	1.5	7.5	113	29	62	89%
3	0	2	1.5	7.5	200	58	55	89%
4	15	2	1.5	7.5	105	44.5	58	95%
5	7.5	1	0	0	130	47	58	94%
6	7.5	1	3	0	255	73	55	85%
7	7.5	1	0	15	80	30	58	95%
8	7.5	1	3	15	110	18.5	64	90%
9	0	1	1.5	0	235	70	58	86%
10	15	1	1.5	0	130	75	56	88%
11	0	1	1.5	15	67	28	75	96%
12	15	1	1.5	15	75	13.1	43	94%
13	7.5	0	0	7.5	85	31.2	62	94%
14	7.5	2	0	7.5	100	36	58	96%
15	7.5	0	3	7.5	88	24	58	94%
16	7.5	2	3	7.5	90	18	50	95%
17	0	1	0	7.5	67	27.5	58	95%
18	15	1	0	7.5	55	54.6	65	97%
19	0	1	3	7.5	230	60	60	87%
20	15	1	3	7.5	73	9	64	95%
21	7.5	0	1.5	0	125	45	55	94%
22	7.5	2	1.5	0	75	24.4	60	95%
23	7.5	0	1.5	15	100	19.5	70	90%
24	7.5	2	1.5	15	70	13.6	48	95%
25	7.5	1	1.5	7.5	85	28.5	62	94%
26	7.5	1	1.5	7.5	87	29.5	65	94%
27	7.5	1	1.5	7.5	60	30.3	55	96%

Table 5. Experimental and Predicted Responses

Std Order/ Run Order	Experimental Values				Predicted Values			
	Penetration	Ductility	Softening point	Elastic Recovery	Penetration	Ductility	Softening point	Elastic Recovery
1	75	34.5	60	95%	93.278	38.3972	61.4167	93.96
2	113	29	62	89%	102.750	30.5375	63.6250	90.92
3	200	58	55	89%	198.167	52.5583	54.7500	87.94
4	105	44.5	58	95%	74.639	36.6986	57.9583	96.90
5	130	47	58	94%	136.972	53.0319	61.6250	92.90
6	255	73	55	85%	239.306	67.8153	55.7917	86.73
7	80	30	58	95%	83.611	31.2806	58.5833	94.13
8	110	18.5	64	90%	90.944	8.5639	61.7500	91.96
9	235	70	58	86%	233.944	67.7306	48.4167	86.91
10	130	75	56	88%	76.056	15.3694	52.5833	93.09
11	67	28	75	96%	40.889	21.5028	59.7500	96.59
12	75	13.1	43	94%	85.778	37.0639	55.5833	97.07
13	85	31.2	62	94%	102.222	22.9361	60.4167	92.93
14	100	36	58	96%	134.111	27.6972	52.2500	92.41
15	88	24	58	94%	77.139	28.1153	59.6250	95.18
16	90	18	50	95%	92.611	55.3056	63.8333	95.13

17	67	27.5	58	95%	204.472	63.1986	59.7917	88.01
18	55	54.6	65	97%	74.944	12.2889	61.0000	93.96
19	230	60	60	87%	134.778	46.4222	53.1667	92.46
20	73	9	64	95%	112.083	23.4042	68.6250	89.14
21	125	45	55	94%	72.306	16.0819	48.4583	95.68
22	75	24.4	60	95%	77.333	29.4333	60.6667	94.67
23	100	19.5	70	90%	77.333	29.4333	60.6667	94.67
24	70	13.6	48	95%	77.333	29.4333	60.6667	94.67

$$\text{Penetration} = 65.2 - 1.50\,\text{Biochar} + 54.8\,\text{WEO} - 12.09\,\text{PA} + 0.998\,\text{PA*PA} - 3.22\,\text{Biochar*WEO} \quad (1)$$

$$\text{Ductility} = 20.2 + 0.52\,\text{Biochar} - 1.96\,\text{PA} + 0.2004\,\text{Biochar*Biochar} + 0.2083\,\text{PA*PA} - 1.736\,\text{Biochar*WEO} - 0.833\,\text{WEO*PA} \quad (2)$$

$$\text{Softening point} = 42.25 + 9.96\,\text{CNSL} - 0.2022\,\text{Biochar*PA} - 0.933\,\text{CNSL*PA} \quad (3)$$

$$\text{ER} = 0.9761 - 0.0337\,\text{WEO} - 0.000640\,\text{PA*PA} + 0.00400\,\text{Biochar*CNSL} + 0.00437\,\text{CNSL*PA} \quad (4)$$

5. RSM STATISTICAL ANALYSIS

RSM statistical analysis is used to assess the significance, interaction, and impact of the IVs on the answers, followed by Analysis of Variance (ANOVA). Equations (1) through (4), which represent polynomial regression and have R2 values of 88%, 93%, 81% and 83% respectively, offer another way to describe the RSM answers. Table 5 shows the experimental and forecasted responses after omitting outliers (Run orders 10,11 & 22 from Table 4) which are physical properties of bitumen (Penetration, Ductility, Softening, and Elastic Recovery) for different IVs. Table 6 shows the ANOVA results for various IVs, along with their p-value as well as their significance. Table 6 demonstrates that items with p 0.05 are considered significant, whereas those with p>0.05 are considered insignificant. Eqs. (1) to (4) of the second-order polynomial regression are purged of the irrelevant terms. Because of their respective p values of 0.023, 0.016, 0.002, 0.012, and 0.05, the linear terms of BC, WEO, and PA, the square term of PA, and the two-way interaction term of BC*WEO have been determined to be the most influential terms in the second-order polynomial Eq. (1) from Eqs. (1) to (4) and Table 5.

The linear and square terms of BC and PA, as well as the two-way interaction terms of BC* WEO and WEO*PA, are the most significant in Eq. (2), with P values of 0.04, 0, 0.019, 0.022, 0.001 and 0.036, respectively.

The linear terms of CNSL and 2-way interaction terms of BC* PA and CNSL*PA are the most significant in Eq. (3), where the P values are 0.032, 0.017, and 0.019 respectively. The linear terms of WEO, square term of PA, and 2way interaction terms of BC* CNSL and CNSL*PA are the most significant in Eq. (4), where the P values are 0.012, 0.021, 0.028, and 0.054 respectively. The responses suggest that the outcomes of the experiment and the forecast correspond rather well. Unknown parameters of a model are estimated using the ordinary least squares approach, which is taken into consideration in Minitab software. Stated differently, its purpose is to determine which line best fits the data points. The strategy is based on lowering the sum of squared residuals between expected and actual values. The residual, usually referred to as an error, is the difference between the actual and expected numbers. A normal probability graph is used to assess the residuals' normal distribution and linearity. A normal probability chart is a visual aid for evaluating the distribution of data and determining its sufficiency. The best-fit line is the diagonal line that spans the data points in this scatter plot of residuals and aids in identifying how the experiment and expected results connect.

The use of a collection of statistical models and the analysis technique known as analysis of variance (ANOVA) to look into the connection between responses and progression variables is summarised in Table 6. The models were fairly adequate, as shown by Table 6, where the p-value (lack of fit) was less than 0.05. One way to evaluate the correctness of the model may be to look at its F values, which are significant at higher levels. Table 6 shows that the models are more significant for the responses of Penetration, Ductility, Softening, and Elastic Recovery, which have F values of 18.68, 53.40, 8.59, and 9.86, respectively. In the model summary, squared shows the overall model fit, S evaluates how well the model explains the response, and Predicted R-squared evaluates a model's capacity to predict future observations and is particularly useful for comparing models with various predictors. Adjusted R-squared also helps with model comparison. It is advised to examine residual plots to verify model assumptions. From the equation, a significant amount of the fluctuation in light output may be explained by the model, according to the R-squared value of 71.80 A substantial amount of the variance in the response variable may be explained by the model, according to the R-squared value of 61. From equation (3), The model appears to explain a significant amount of the variance in the response variable, based on the R-squared value of 80.53%.

The residuals versus fits plot can be used to confirm whether the residuals are distributed at random and have a constant variance. The points should ideally fall arbitrarily on either side of 0, with no discernible patterns.

5.1. Interpretation of contour plots

Based on the shape of the contour plots the following can be interpreted, if the shape of the contour plot comprises a Circle or Ellipse, it can be stated that the contour is well-behaved, a quadratic response surface, and if the shape is Asymmetrical, it suggests interaction effects between variables. The following contour plots fall under Circle or Ellipse i.e., from Penetration, PA*Biochar and WEO*CNSL, from Ductility, PA*Biochar, from Softening point, WEO*CSNL, from Elastic Recovery, PA*Biochar & WEO*CNSL. All the remaining contour plots from Penetration, Ductility, Softening Point, and Elastic Recovery fall under Asymmetrical.

Based on the spacing of the contour lines the following can be interpreted, Closed contours represent steep slopes or rapid changes in the response and Wider contours represent flatter regions where the change takes place slowly. The following contour plots represent Closed spacing i.e., from Penetration, PA*Biochar, from Ductility, PA*Biochar, and Elastic Recovery, PA*Biochar. The rest of the contours are widely spaced.

In Figure 2, the contour plot shows the relationship between various combinations of the factors influencing the penetration of Bio Bitumen. Lighter regions indicate higher quality. The following optimal percentage of the mix are observed between CNSL vs Biochar as 0% – 0.3% & 0% - 15%, WEO vs Biochar as 0% - 0.7% & 0% - 15%, PA vs Biochar as 5% - 15% & 3% - 15%, WEO vs CNSL as 0% - 0.5% & 0% - 0.8%, PA vs CNSL as 3% - 14% & 0% - 2% and PA vs WEO as 0% - 3% & 0% - 3%. This contour plot shows the relationship between various combinations of the factors influencing the ductility of Bio Bitumen. Lighter green regions indicate higher quality (The quality increases as the green turns from lighter to darker). The following optimal percentage of the mix are observed between CNSL vs Biochar as 0.3% – 2% & 0% - 3%, WEO vs Biochar as 0.95% - 3% & 0% - 4% as well as 0% - 1% & 11% - 15%, PA vs Biochar as 0% - 15% & 0% - 15% and varies as shown in the plot, PA vs CNSL as 0% - 5% & 0% - 2% and varies curvilinearly as shown in plot and PA vs WEO as 0% - 3.5% & 0% - 3% varies curvilinearly as shown in the plot. This contour plot shows the relationship between various combinations of the factors influencing the softening point of Bio Bitumen.

Green regions except where the value is < 50 indicate higher quality (The quality increases as the green turns from lighter to darker). This contour plot shows the relationship between various combinations of the factors influencing the elastic recovery of Bio Bitumen. The optimum value of ER is 75% and after interpreting the above plots all the plots are within the optimal range.

5.2. Residual Plots

From the graph, figure 4, the following can be inferred, The Normal Probability Graph of all the responses follows the normal distribution approximately around the straight line, showing a linear connection with fewer Outliers. In all the graphs, the Histogram follows the trend of the Normal Probability Graph supporting its pattern of distribution. From the Residual vs Fits graphs of all the responses, the following can be understood the distribution of Positive and Negative residuals above and below the straight line are almost the same and hence state the equality in the variance in the data. From the residual vs Order graphs of all the responses, the following can be drawn that is all points in the data sets do not follow any specific order in the experiment and all data points are independent of each other.

5.3. Lack of Fit (P Value) and Pareto Analysis

The P value is used to determine the relevance of progression factors. The model's P value is the F test's possibility value, which should be as low as possible. If the P value of the development variable is 0.05 or 0.01, the progression variable is considered considerable. If the progression variable's p-value is more than 0.05, it is considered unimportant. According to ANOVA Table 6, the P values of PA, PA*PA, WEO, BC, and WEO*BC for Penetration were less than 0.05, but the p values of the rest of the model's linear, quadratic, and 2-way interactions were greater than 0.05. When the CNSL is included, the influence is insignificant, and the P value of both the linear CNSL as well as the quadratic CNSL*CNSL is more than 0.05, indicating that the CNSL has a lower relevance in Penetration. According to the Pareto chart in Figure 5, the values of BC, PA, BC*BC, PAPA, BC WEO, and WEO PA were less than 0.05, indicating their impact on the model's ductility, although the p values of the linear, quadratic, and 2-way interaction of the rest of the model were greater than 0.05. While the P values of linear CNSL and WEO do not affect the model's ductility. The CNSL, BC PA, and CNSL*PA P values for the Softening Point were significant since the Lack of fit was less than 0.05, but the p values of the linear, quadratic, and 2-way interaction of the rest of the model were greater than 0.05. Considering the P values of linear BC, WEO, and PA does not affect the model’s Softening point. P values of WEO, PA*PA, BC*CNSL, and CNSL*PA for Elastic Recovery were significant since the Lack of fit is less than 0.05, but the p values of the linear, quadratic, and 2-way interaction of the rest of the model were higher than 0.05. While considering the P values of linear BC, CNSL & PA do not have any influence on the Elastic Recovery of the model.

Table 6: ANOVA for Penetration, Ductility, Softening Point, and Elastic Recovery

Analysis of Variance Source	Penetration (dmm)			Ductility (cm)			Softening Point (oC)			Elastic Recovery (%)		
	DF	F-Value	P-Value	DF	F-Value	P-Value	DF	F-Value	P-Value	DF	F-Value	P-Value
Model	14	4.68	0.013	14	8.4	0.002	14	2.71	0.068	14	2.97	0.053
Linear	4	10.79	0.002	4	17.98	0	4	2.09	0.164	4	4.96	0.022
Biochar	1	7.55	0.023	1	5.79	0.04	1	1.2	0.301	1	3.92	0.079
CNSL	1	3.54	0.093	1	4.39	0.066	1	6.45	0.032	1	0	0.99

WEO	1	8.82	0.016	1	0.82	0.389	1	0.37	0.559	1	9.86	0.012
PA	1	18.68	0.002	1	53.4	0	1	0.28	0.612	1	3.71	0.086
Square	4	2.5	0.116	4	2.79	0.093	4	0.76	0.574	4	2.01	0.176
Biochar*Biochar	1	3.4	0.098	1	8.13	0.019	1	0.51	0.492	1	2.68	0.136
CNSL*CNSL	1	0.38	0.555	1	0.11	0.752	1	2.21	0.171	1	0.07	0.802
WEO*WEO	1	0.08	0.783	1	0.08	0.79	1	0.33	0.58	1	0.11	0.745
PA*PA	1	9.85	0.012	1	7.61	0.022	1	0.01	0.924	1	7.84	0.021
2-Way Interaction	6	2.55	0.1	6	6.32	0.008	6	2.78	0.082	6	2.37	0.118
Biochar*CNSL	1	4.32	0.067	1	0.28	0.611	1	0.02	0.898	1	6.82	0.028
Biochar*WEO	1	5.14	0.05	1	26.43	0.001	1	0.16	0.702	1	1.7	0.224
Biochar*PA	1	0.08	0.785	1	1.97	0.194	1	8.59	0.017	1	0.14	0.714
CNSL*WEO	1	0.04	0.843	1	0.51	0.495	1	0.28	0.612	1	0.05	0.833
CNSL*PA	1	3.58	0.091	1	3.18	0.108	1	8.13	0.019	1	4.88	0.054
WEO*PA	1	2.21	0.172	1	6.09	0.036	1	1.4	0.267	1	0.76	0.407

*Bold indication represents the P values < =0.05 which are considered as Significance

Table 7: D-Optimal values and corresponding responses

D- Optimal	BC	CNSL	WEO	PA	Penetration	Ductility	Softening Point	Elastic Recovery
84.27	15%	1.71%	0%	4.54%	4.96mm	28cm	58	92%
80.34	15%	1.71%	0%	7.5%	4.16mm	25cm	60	94%

Table 8. Physical properties of virgin bitumen and biochar-modified bitumen

Type of Bitumen	Penetration (dmm)	Softening (oC)	Ductility (cm)	Penetration Index (PI)	PRR %	SPI	RD	ER (%)	SS(ºC)
Base bitumen	52.3	50	70	-1.095747242	NA	NA	NA	NA	NA
Base+ 5% BC	62.5	58	47	1.204101573	119.5	8	67.14		
Base+ 10% BC	56	60	83	1.32135307	107.0	10	118.5		
Base+ 15% BC	44	62	59	1.102013292	84.13	12	84.28	79	4
Base+ 20% BC	65	62	75	2.129976764	124.2	12	107.14		
Base+ 25% BC	59	62	77	1.857466995	112.8	12	110		
Base + 2.5% CNSL	147.3	52	90	2.707006149	281.6	2	128.57		
Base + 5% CNSL	306	40	70	2.545852293	585.0	-10	100		
Base + 10% CNSL	306.6	-	-		586.2				
Base + 15% CNSL	322	-	-		615.6				

5.4. Surface Plots

Because the model incorporates statistically significant quadratic factors, the response surface is curved. Various combinations were generated among the four responses. From Figure 6, it can be inferred that an increase in both Biochar and CNSL to their max values, provides less value of Penetration, while the absence of CNSL and Biochar at its maximum, provides unusual Penetration values. The same can be interpreted from the Biochar & WEO surface plot. The relation between Biochar and PA states that the optimum values of Penetration can be obtained only when they are at their maximum levels. From the CNSL & WEO surface plot, it can be observed that the levels of both CNSL and WEO, from 0% - 1.5% and 0% - 1.85% respectively, give the optimum values of Penetration, while increasing them to their fullest levels provides unusual Penetration value. From CNSL and PA surface plots, it can be inferred that Optimum Penetration can be obtained when they are at their maximum level of percentage. From the WEO & PA, the Lowest values of Penetration can be observed when WEO & PA are at 0% & 16% and 3% & 16% respectively.

From Figure 6, between Biochar & CNSL it can be inferred that the optimum Ductility value = > 40 is obtained when Biochar & CNSL are at 14% & 2% respectively as well as when the Biochar is at 0% & CNSL beyond 0.5%. From Biochar & WEO, the optimum value of Ductility can be obtained when Biochar & WEO are at 0% & 1.75% respectively and the Ductility reduces when the Biochar is beyond 6% and when WEO is less than 1.75%. From Biochar & PA, the optimum Ductility can be obtained when Biochar & PA at 0% & (7% - 16%) and it increases by increasing Biochar from 8% - 16% and PA at 10%. From CNSL & WEO the maximum Ductility obtained is approximately 26 and at CNSL between 1% & 1.5% and WEO at its maximum. From CNSL and PA, it can be inferred that the optimum value of Ductility can be obtained when approximately PA is at 4% - 6% and CNSL at 0% - 1.8% approximately. From WEO & PA, it can be inferred that better results can be obtained when PA is kept at 0% and WEO can be utilized from 0% - 2% approximately.

From Figure 6, it can be inferred that from Biochar & CNSL the Optimum value of Softening Point can be obtained when Biochar and CNSL are at (0% - 8%) approximately & 2% respectively. From the Biochar and WEO plot, it can be inferred that the Softening point obtained is between 55 and 60 when the Biochar is at 0% and WEO is at 0% & 3%. From Biochar and PA, it can be observed that the Softening point is less than 50 when both the values are at 0%, further increase in their percentages, increases the softening point value beyond the limit. From CNSL and WEO it can be understood that the softening point is optimal when both CNSL & WEO are at their fullest, while the reduction in their percentage leads to the increased value of the softening point. From CNSL and PA, it can be observed that the softening point is optimum when both the CNSL & PA are at their maximum values. From WEO and PA, the softening point can be said to be between 55 & 57.5, when WEO and PA are at 3% & 0% respectively.

From Figure 6, it can be inferred that all the samples have Elastic Recovery of more than 85% which is in line with the standards, IRC: SP:53-2002. Figure 6, 3D surface plots, aid in illustrating the variance trend and the impact of various independent variables (IVs) on variables that are dependent (DVs). All of the responses from these figures (Penetration, Softening, Ductility, and Elastic Recovery) are depicted on the Z-axis, while the IVs are plotted on the axes of X and Y. Surface plots are generated as functions of the first two IVs while keeping the third IV constant.

Table 9. Asphaltenes and Maltenes fractions of bitumen

Name of the bitumen	Asphaltenes (%)	Maltenes (%)
Base bitumen	21.69	78.31
D-optimal 1	50.5	49.5
D-optimal 2	45.37	54.63

5.5. D-Optimal Analysis

Figure 3, Optimisation of mix from the D optimum graph D-optimal is used in RSM to optimize the Bio Bitumen mix proportions. Table 6 lists the factors for achieving the best Penetration, Ductility, Softening Point, and Elastic Recovery. For this desired target Penetration is set to the minimum and Ductility, Softening Point, and Elastic Recovery are set to the maximum values of experimental responses for this intended objective. Figure 3 depicts the optimized Penetration, Ductility, Softening Point, and Elastic Recovery IVs settings at BC=15%, CNSL-1.7172%, WEO-0%, and PA=4.5455%.

The symbols 'y' and 'd' denote maximum penetration, ductility, softening point, and elastic recovery, as well as the usefulness of IVs. The value of 'd' ranges from 1 to 0, indicating the most desirable and least desirable. According to Figure 5, the optimal composite desirability is d=0.8427, with response desirability at d=0.657 for penetration, d=0.979 for Ductility, d=0.917 for Softening point, and d=0.852 for Elastic, indicating that the optimal IV's as per Table 7 are most desirable for all responses except Penetration, which is less than 0.80.

To enhance the desirability of Penetration value, different iterations were performed, and it was found that altering the value of PA from 4.5455% to 7.5% delivers the composite desirability of d = 0.8034, with desirability of Penetration d = 0.894, Ductility d = 0.779, Softening Point d = 0.598 and for Elastic Recovery d = 1. Even though the d values for Ductility and Softening Point are less than 0.80 in the second run, they are considered because y values are in line with Indian Bitumen Specifications as Per IS 73:2006.

5.6. Model validation

The model is validated by running the experiment analysis based on the ideal quantities of IVs, as illustrated in Figure 5. The experimental results outperform the model predictions and are consistent with Indian Bitumen Specifications as per IS 73:2006, as shown in the table below.

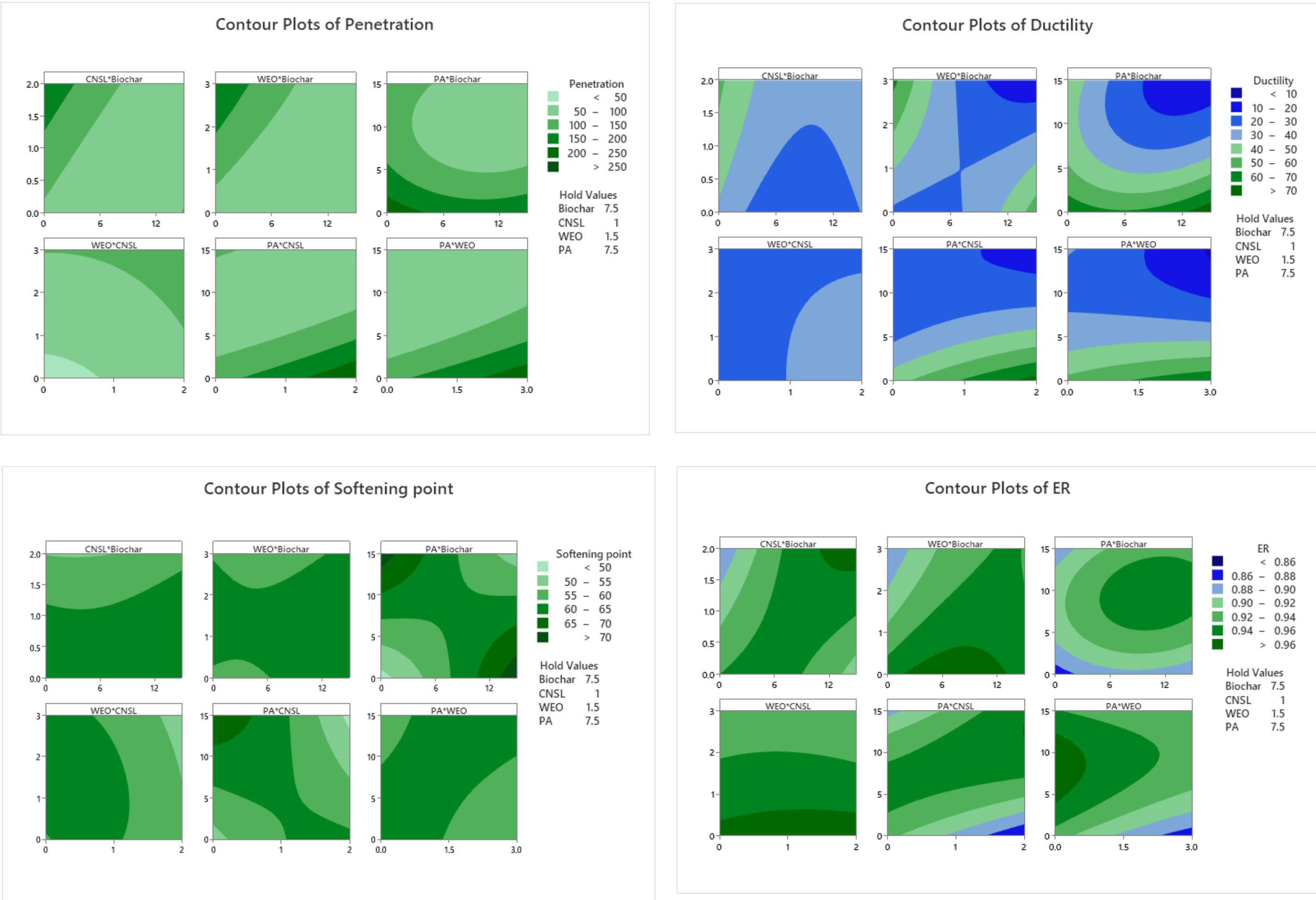

Figure 2. Contour Plots for Responses (Penetration, Ductility, Softening point, and Elastic Recovery)

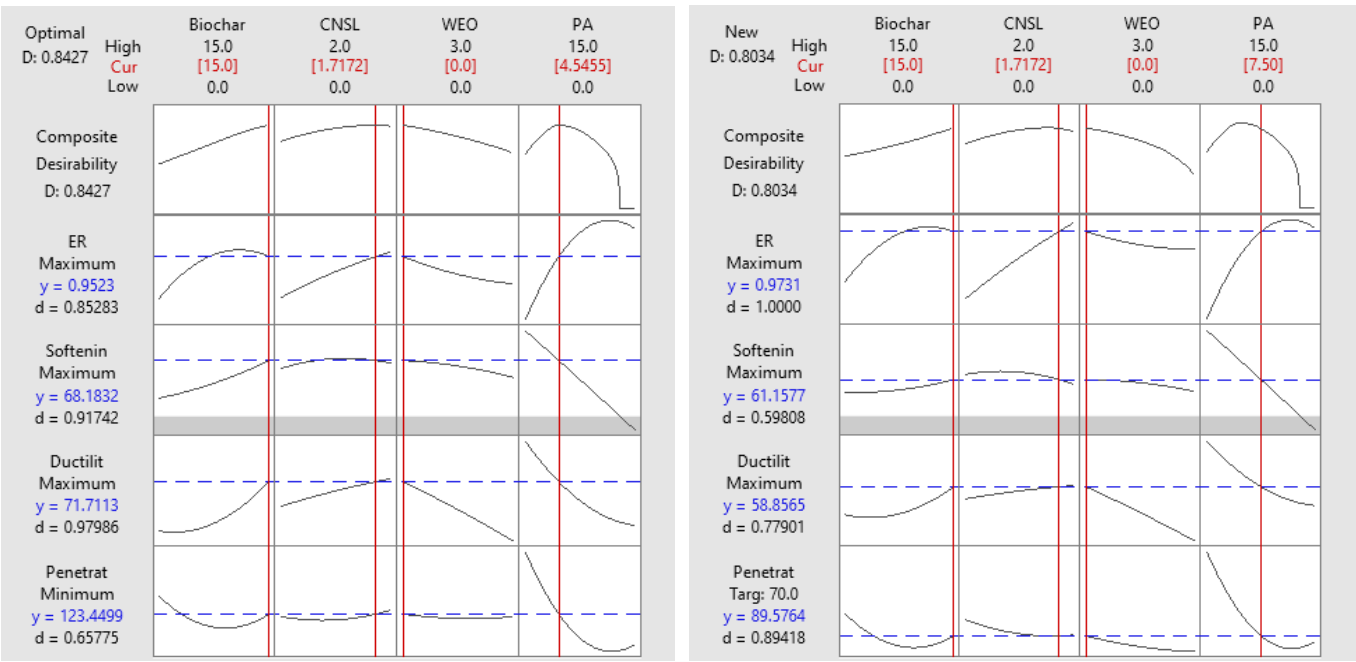

Figure 3. D-optimal graphs from the response surface method

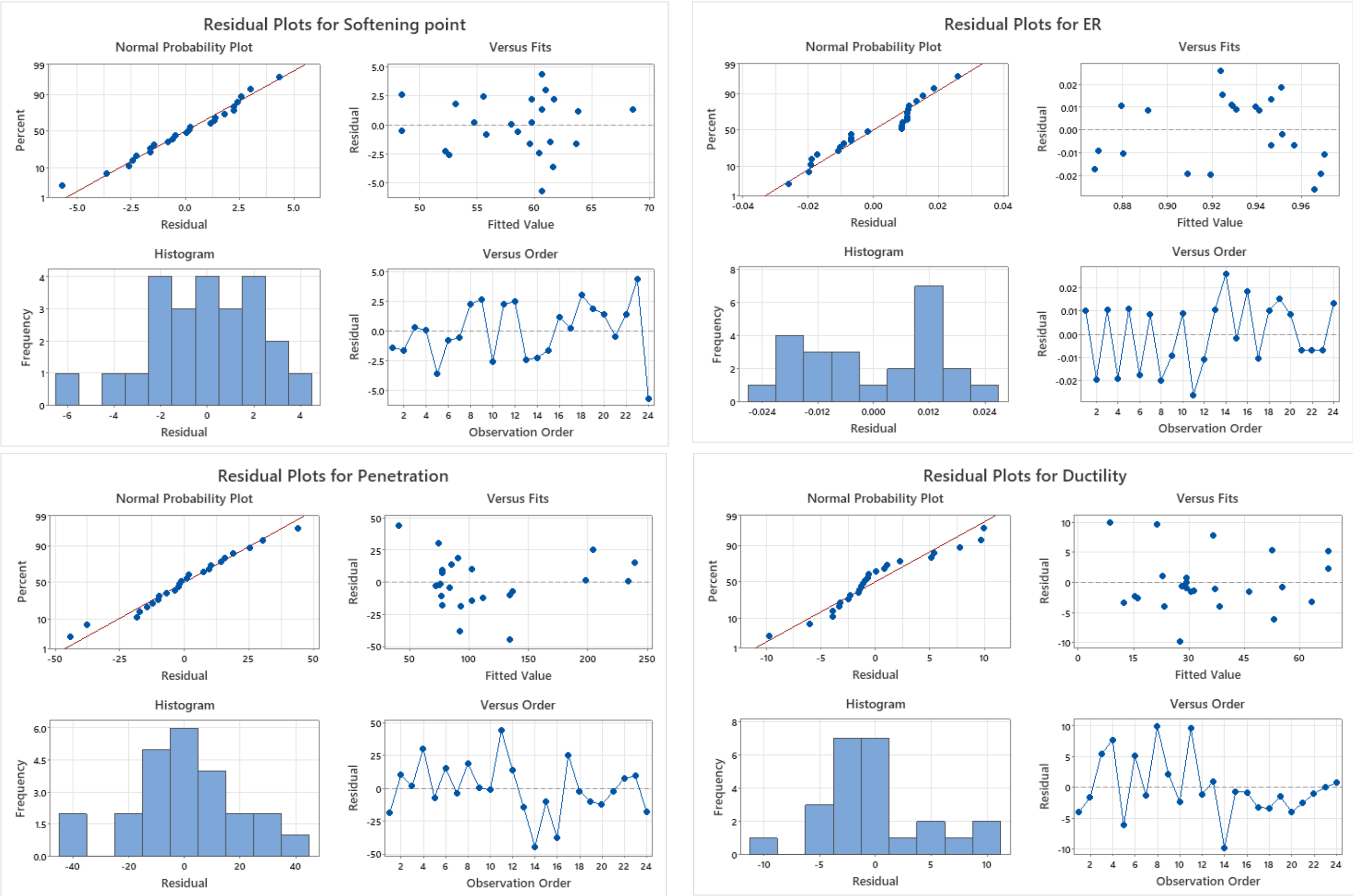

Figure 4. Residual Plots for responses (Penetration, Ductility, Softening point, and Elastic Recovery)

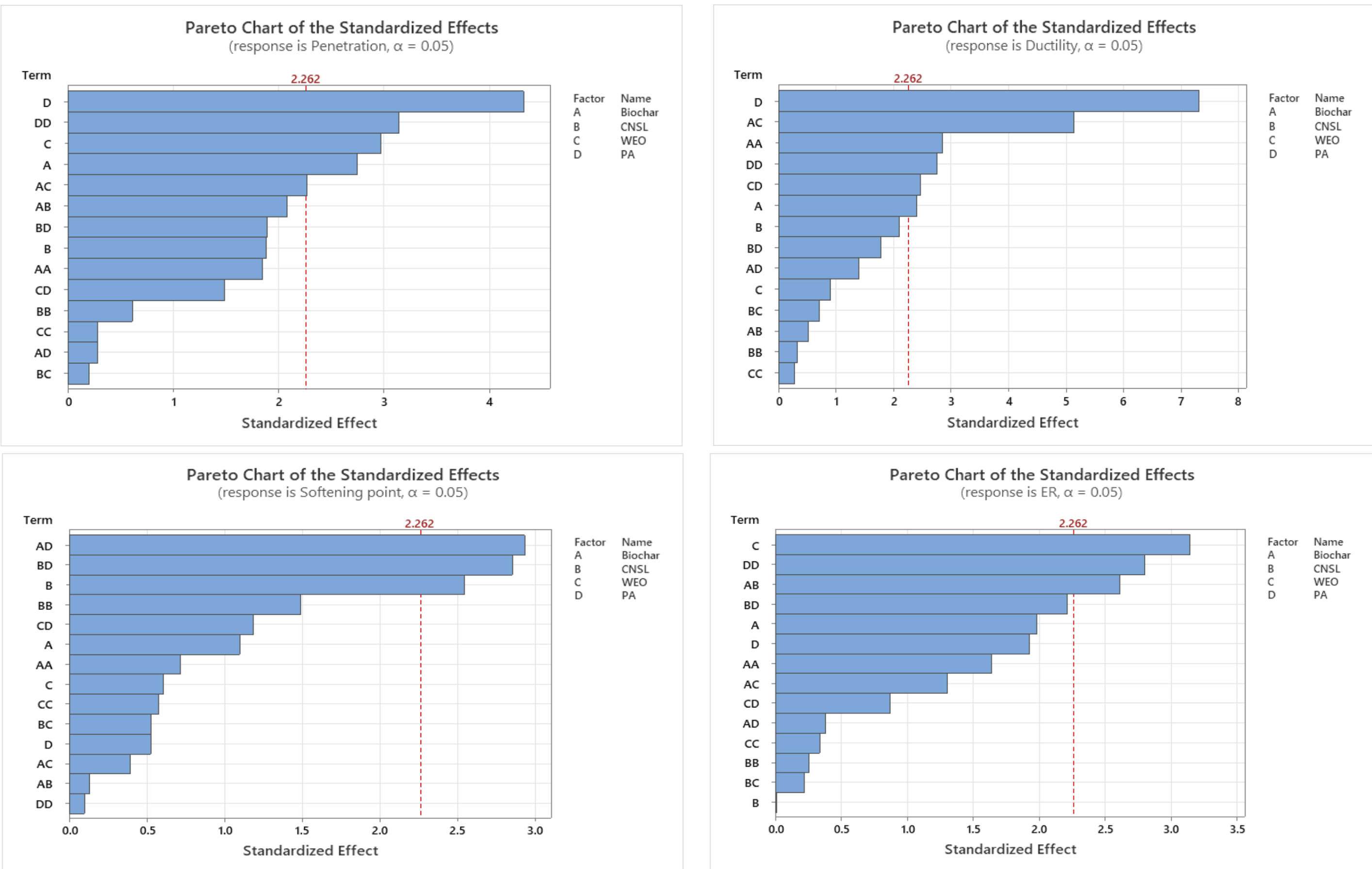

Figure 5. Pareto plots for responses (Penetration, Ductility, Softening point, and Elastic Recovery)

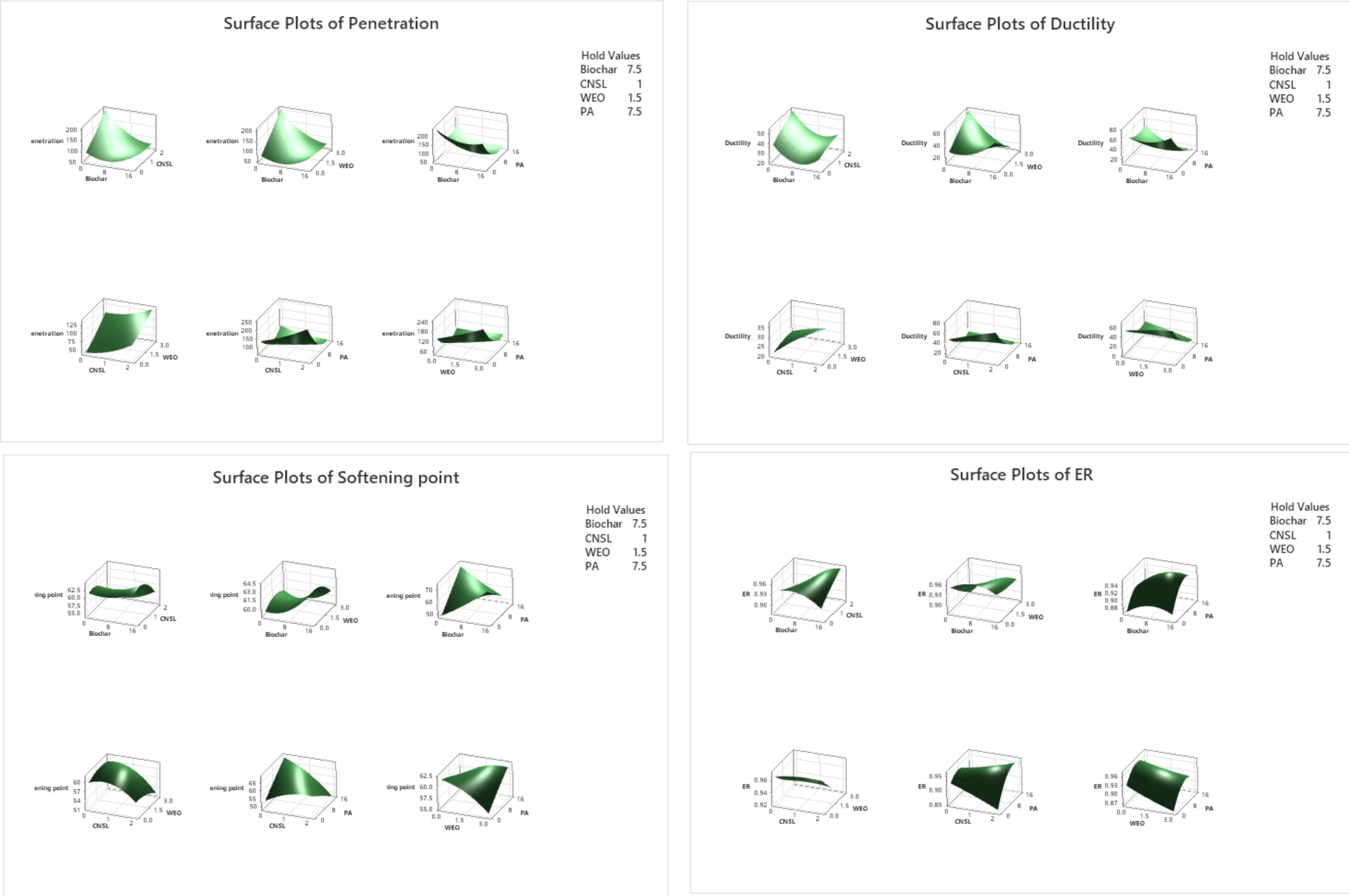

Figure 6. Surface plots for responses (Penetration, Ductility, Softening point, and Elastic Recovery)

5.7. *Effects of CNSL and BC addition on physical properties*

Impact of CNSL and BC addition on physical attributes: Table 8 displayed the physical characteristics of the basic and modified binders. The findings show that adding BC to the base binder reduced penetration values, which for 15%BC ranged from 53dmm to 44dmm. It shows that the use of BC stiffened the binder, greatly increasing its ability to resist rutting. When 15% BC was added to the base binder, the softening point of the modified BC binders increased to 62C, whereas the base binder only showed a softening point of 50C. This suggests that the binder that has been changed with BC will be more resistant to temperature susceptibility. As a result of a binder stiffening, the ductility value of BC-modified binders dropped as the BC concentration increased. The ductility value for the 15%BC modified binder, however, is 59 cm, which is greater than the 40 cm minimum needed for VG 30-grade bitumen. Using the Pfeiffer and Van Doormaal formula, the penetration index (PI) of the basic and modified binders was determined based on equations from the literature. An increase in BC content has resulted in higher binders' PI values. For binders that were extremely temperature sensitive, the PI range was -3; for binders that were extremely low temperature sensitive, it was +7.

The adjusted binders' PI fell within the desired range. The generalized equations were used from the literature to compute the penetration retention rate, retained ductility, softening point incremental, and the impacts of adding BC and CNSL to bitumens' physical characteristics. It is evident from the above table that adding 15% BC to base bitumen has a greater impact on physical qualities than adding 0–10%. For BC 15%, a 30% PPR decrease was noted; this is also the lowest number. The softening point increment demonstrated a linear relationship with the rise in the percentage of BC. The bitumen's retained ductility has reduced BC contents by 5% and 15%. This makes it clear that adding 0–10% BC has had a little smaller impact on physical attributes than adding 15% BC, which has had a considerable impact.

6. CHARACTERISATION FOR THE OPTIMUM BLENDING COMPOSITION

After obtaining D-optimal results, asphalt binders were chemically characterized via SARA fractionation (saturates, aromatics, resins, and asphaltenes). Bitumen comprises two chemical fractions, namely, asphaltenes and maltenes, which are solid and liquid/oil phases, respectively. The maltenes fraction is further classified into three phases, namely, resins, aromatics, and saturates, with SARA representing the increasing order of hydrocarbons. The Corbett method was used in this investigation to separate the asphaltenes and maltenes fractions. This method involves taking approximately 10 grams of bitumen in an Erlenmeyer flask and adding 100 ml of n-heptane per gram of bitumen The sample was agitated while n-heptane was added and permitted to stand overnight. Following that, the mixture was vacuum filtered through Whatman grade-1 filter paper, and the particles remained on the paper after being dried and weighed as asphaltenes, as shown in Figure 7. The remaining substance, after removing n-heptane from the liquid phase, is referred to as maltenes (Sandeep et al., 2021). The storage stability test was carried out in this work using the Standard Test Methods of Bitumen and Bituminous Mixtures for Highway Engineering in China (JTG E20-2011) [25].

Following the manufacturing of the modified asphalt binder, the binder was heated at 170 °C for 2 hours to achieve adequate fluidity. The asphalt binder, weighing 50 g, was then put into a glass test tube (25 mm in diameter and 200 mm in height). The tube was covered with a tube plug and placed vertically in a 163°C oven for 48 hours. After being stored at high temperatures, the tube was refrigerated at -10°C for a further four hours. After that, a glass cutter was used to cut the asphalt binder sample into three equal-length pieces. The upper and lower halves were collected individually and put inside an inverted container. After that, the container was heated to 163°C in an oven to make sure the asphalt binder was released from the glass tube that opened. After taking the empty glass tube out of the container, the asphalt binder was added to the MSCR and softening point molds in preparation for additional testing (Han et al., 2022).

The resilience of modified asphalt under high temperatures was evaluated by a hot storage test. 50g of hot nano clay-modified asphalt containing WAA has been placed within an aluminum tube measuring 25 mm in diameter and 140 mm in height. The material was then kept in a vertical jar at 163 ± 5°C for 48 ± 1 hour After that, it was removed and placed in a freezer at -6.7pm50c for at least 4 hours to completely harden the sample. Lastly, the tube was divided into three equal parts. To investigate probable differences in features, the two ends (top and bottom) were further analyzed using the ring and ball softening point test (ASTM D 36), to evaluate possible differences in characteristics If the difference in softening point between the top and bottom parts of the tube is less than 2.2°C, the sample may be considered a storage stable mix, which is a critical parameter of initial qualities on modified asphalt mixes (ASTM D5926) (Abdullah et al., 2012).

Figure 7. SARA analysis and Storage stability test

7. CONCLUSIONS

The goal of this study is to optimize conventional bitumen by introducing four various inputs Biochar, CNSL, WEO, and PA. For this study, the RSM statistical analysis approach has been modified using the Box Behnken Method. The conclusions that follow can be taken from the research and experiments: From the D optimal graph, the optimum values obtained are BC – 15%, CNSL – 1.72%, WEO – 0%, and PA – 4.54% for the D optimal Value of 84.27%, but the results obtained for penetration did not meet the standard value. Then the optimum values are obtained, after raising the PA value from 4.54% to 7.5%, the optimal values are reached, and it can be stated that it has a substantial effect on penetration without affecting the composite optimum value.

•From the D optimal results, it can be concluded that WEO does not have any significant effect on the model for any of the responses studied.
•The relation between experimental and predicted values are mostly in line with each other since there are 3 outliers, hence they are omitted to enhance the model efficiency.
•From the Pareto charts, it can be understood that penetration and ductility required more linear terms than Softening point and Elastic recovery.
•Since the model comprises Phthalic Anhydride, it is required to carry out further research to make it cost-effective.
•With the help of Contour plots, the curves show a well-behaved quadratic response surface and interaction effects between variables. The optimal percentage of the mix is found between CNSL vs Biochar, WEO vs Biochar, PA vs Biochar, PA vs Biochar, and green regions show higher quality.
•From the surface plots, the model incorporates quadratic factors, resulting in a curved response surface. The results show that increasing Biochar and CNSL results in less penetration value, while the absence of CNSL and Biochar results in unusual penetration value. The optimum penetration values are obtained when Biochar and CNSL are at their maximum levels, while the optimum ductility value is obtained when Biochar and PA are at 0% and 1.75%.
•It is evident from the experimental findings, as displayed in the table, that bitumen's asphaltene content has grown when BC, CNSL, and PA content have increased. The transformation of resins into asphaltenes might be the cause of the rise in asphaltene concentration. Furthermore, there was a drop in the maltene fractions, which might be explained by the transfer of aromatics and saturates to resins.
•The study examined the effects of Biochar (BC) and Cashew Nut Shell Liquid (CNSL) addition on the physical properties of base and modified binders. Results showed that the addition of 15% BC to the base binder decreased the penetration value, indicating stiffening, and increased resistance to temperature susceptibility. The softening point of BC-modified binders increased with increasing BC content, with 15% BC showing a softening point of 62oC. The ductility value decreased with increasing BC content, but the 15% BC modified binder had a ductility value of 59cm, exceeding the minimum requirement of 40 cm for VG 30 grade bitumen.

•The softening point range found in storage stability testing is 3 to 5 oC. The findings thus agree with the standards of current literature.
•It is significant to note that the penetration grade of 60/70 was obtained in the laboratory test, although the d-optimal model anticipated an 80/100 grade. This discrepancy points to possible restrictions on the accuracy of the model or minute changes in the material's characteristics during testing. Larger-scale testing for additional validation might yield insightful information for improving the RSM model and guaranteeing the findings' practical applicability.
•The RSM study revealed that, despite the bitumen modification efficacy of biochar, CNSL, WEO, and PA individually, 0% WEO was in the optimal combination because of possible antagonistic interactions or chemical incompatibility. RSM takes into account these elements as well as synergistic effects to determine the best mix of modifiers that will result in the best bitumen characteristics. Put another way, while WEO could be useful on its own, it might not work well with the other modifiers selected in this particular instance.
•More investigation is required to guarantee the broad use of bio-bitumen in sustainable pavements. This comprises practical trials in road-building projects as well as extensive testing of the optimized mix (chemical composition, rheological behavior, morphology, degree of cross-linking, and life cycle analysis). Further research into different bio-based additives or waste materials might result in even more environmentally acceptable and highly effective bio-bitumen compositions.

ACKNOWLEDGMENTS

We would like to thank the B.Tech students from GMRIT, Rajam, AP, India, namely Narayanam Venkata Sai Manikanta, R Rajasekhar, N Sai Prasanna, Boyina Sai Deekshith, Potnuru Geethika, and M Dilleshwarao, for their excellent assistance with the laboratory experiments. Their help was crucial in getting this research finished. We also like to express our gratitude to Narayanam Venkata Sai Manikanta for his unwavering encouragement during the whole undertaking.

REFERENCES

Abdullah, M., Zamhari, K., Nayan, N., Hainin, M., & Hermadi, M. (2012). Physical properties and storage stability of asphalt binder modified with nano clay and warm asphalt additives. World Journal of Engineering, 9(2), 155–160.
DOI: 10.1260/1708-5284.9.2.155

Anupam, K., Akinmade, D., Kasbergen, C., Erkens, S., & Adebiyi, F. (2023). A state-of-the-art review of Natural bitumen in pavement: Underlining challenges and the way forward. Journal of Cleaner Production, 382, 134957.
DOI: 10.1016/j.jclepro.2022.134957

Aydar, A. Y. (2018). Utilization of Response Surface Methodology in Optimization of Extraction of Plant Materials. In Statistical Approaches with Emphasis on Design of Experiments Applied to Chemical Processes. InTech.
DOI: 10.5772/intechopen.73690

Caputo, P., Abe, A. A., Loise, V., Porto, M., Calandra, P., Angelico, R., & Oliviero Rossi, C. (2020). The Role of Additives in Warm Mix Asphalt Technology: An Insight into Their Mechanisms of Improving an Emerging Technology. Nanomaterials, 10(6), 1202.
DOI: 10.3390/nano10061202

De Feo, G., Ferrara, C., Giordano, L., & Ossèo, L. S. (2023). Assessment of Three Recycling Pathways for Waste Cooking Oil as Feedstock in the Production of Biodiesel, Biolubricant, and Biosurfactant: A Multi-criteria Decision Analysis Approach. Recycling, 8(4), 64.
DOI: 10.3390/recycling8040064

Emtiaz, M., Imtiyaz, M. N., Majumder, M., Idris, I. I., Mazumder, R., & Rahaman, M. M. (2023). A Comprehensive Literature Review on Polymer-Modified Asphalt Binder. CivilEng, 4(3), 901–933.
DOI: 10.3390/civileng4030049

Fei, W., Opoku, A., Agyekum, K., Oppon, J. A., Ahmed, V., Chen, C., & Lok, K. L. (2021). The Critical Role of the Construction Industry in Achieving the Sustainable Development Goals (SDGs): Delivering Projects for the Common Good. Sustainability, 13(16), 9112.
DOI: 10.3390/su13169112

Gürer, C., Elmacı, A., Alagöz, O., & Yılmaz, N. (2020). Rheological behavior of bituminous binders replaced by poppy capsule pulp-based bio-oil. Construction and Building Materials, 264, 120631.
DOI: 10.1016/j.conbuildmat.2020.120631

Ibrahim, S. H., Ibrahim, N. I. A., Wahid, J., Goh, N. A., Koesmeri, D. R. A., & Nawi, M. N. M. (2018). The Impact of Road Pavement on Urban Heat Island (UHI) Phenomenon. International Journal of Technology, 9(8), 1597.
DOI: 10.14716/ijtech.v9i8.2755

Ingrassia, L. P., Lu, X., Ferrotti, G., & Canestrari, F. (2019). Renewable materials in bituminous binders and mixtures: Speculative pretext or reliable opportunity? Resources, Conservation and Recycling, 144, 209–222.
DOI: 10.1016/j.resconrec.2019.01.034

Jegan, J., Praveen, S., Pushpa, T. B., & Gokulan, R. (2020). Biodecolorization of Basic Violet 03 Using Biochar Derived from Agricultural Wastes: Isotherm and Kinetics. Journal of Biobased Materials and Bioenergy, 14(3), 316–326.
DOI: 10.1166/jbmb.2020.1969
Joseph, M. S., & C S, B. (2023). Potential of Cashew Nut Shell Liquid as S Sustainable Organic Additive to Improve the Moisture Damage Resistance of Warm Mix Asphalt. SSRN Electronic Journal.
DOI: 10.2139/ssrn.4512289

Kumari, M., & Gupta, S. K. (2019). Response surface methodological (RSM) approach for optimizing the removal of trihalomethanes (THMs) and their precursors by surfactant-modified magnetic nano adsorbents (SNMP) - An endeavor to diminish probable cancer risk. Scientific Reports, 9(1), 18339.
DOI: 10.1038/s41598-019-54902-8

Larter, S. R., & Head, I. M. (2014). Oil Sands and Heavy Oil: Origin and Exploitation. Elements, 10(4), 277–283.
DOI: 10.2113/gselements.10.4.277

Li, H., Dong, B., Wang, W., Zhao, G., Guo, P., & Ma, Q. (2019). Effect of Waste Engine Oil and Waste Cooking Oil on Performance Improvement of Aged Asphalt. Applied Sciences, 9(9), 1767.
DOI: 10.3390/app9091767

Lu, Z., Qiu, R., Zhang, B., & Wang, L. (2023). The synergistic effect of waste engine oil and organic montmorillonite on properties of bitumen: Conventional, high-temperature rheological, and self-healing. Construction and Building Materials, 364, 129946.
DOI: 10.1016/j.conbuildmat.2022.129946

Mohd Hasan, M. R., Chew, J.-W., Jamshidi, A., Yang, X., & Hamzah, M. O. (2019). Review of sustainability, pretreatment, and engineering considerations of asphalt modifiers from industrial solid wastes. Journal of Traffic and Transportation Engineering (English Edition), 6(3), 209–244.
DOI: 10.1016/j.jtte.2018.08.001

Saleem, M. (2022). Possibility of utilizing agriculture biomass as a renewable and sustainable future energy source. Heliyon, 8(2), e08905.
DOI: 10.1016/j.heliyon.2022.e08905

Siddiqua, A., Hahladakis, J. N., & Al-Attiya, W. A. K. A. (2022). An overview of the environmental pollution and health effects associated with waste landfilling and open dumping. Environmental Science and Pollution Research, 29(39), 58514–58536.
DOI: 10.1007/s11356-022-21578-z

Tabaković, A., van Vliet, D., Roetert-Steenbruggen, K., & Leegwater, G. (2023). Bio-Oils as Asphalt Bitumen Rejuvenators. MAIREINFRA 2023, 27.
DOI: 10.3390/engproc2023036027

Tao, X., Yang, K., Cai, M., Luo, J., Li, X., Wu, S., & Cheng, C. (2023). Research on the Rheological Properties and Anti-Aging Mechanism of Paper-Black-Liquor-Modified Bitumen. Sustainability, 15(16), 12356.
DOI: 10.3390/su151612356

Zhou, T., Dong, Z., Wang, P., Yang, C., & Luan, H. (2020). Incorporating chemical acids to react with bio-oil: Hydrophobicity improvement and effect on the moisture susceptibility of bio-binder. Construction and Building Materials, 255, 119402.
DOI: 10.1016/j.conbuildmat.2020.119402

Zhu, J., Birgisson, B., & Kringos, N. (2014). Polymer modification of bitumen: Advances and challenges. European Polymer Journal, 54, 18–38.
DOI: 10.1016/j.eurpolymj.2014.02.005