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Evaluation of pyrolysis products from pine cones as additives for bituminous binders

Çam kozalaklarından elde edilen piroliz ürünlerinin bitümlü bağlayıcı katkı maddesi olarak değerlendirilmesi

İbrahim Aslan[1] *, Yüksel Taşdemir[2]

[1] *Yozgat Bozok University, Institute of Hemp Research, 66100, Yozgat, Türkiye*
[2] *Yozgat Bozok University, Civil Engineering Department, 66100, Yozgat, Türkiye*

Abstract

This research examined the impact of biochar and bio-oil, derived from the pyrolysis process of pine cones, on a bituminous binder. The bituminous binder underwent modification by including biochar at concentrations of 5%, 10%, and 15%, as well as bio-oil at concentrations of 2%, 4%, and 6%. The penetration, softening point, rotational viscometer (RV), and dynamic shear rheometer (DSR) tests were conducted to examine the physical and rheological characteristics of both natural and modified bituminous binders. The binders' temperature sensitivity and rutting resistance were assessed based on the data acquired from the testing. The study concluded that including pyrolytic materials, namely biochar and bio-oil derived from pine cones, as additives in bituminous binders may effectively reduce the temperature sensitivity of the binder and enhance its resistance to rutting.

Keywords: Bituminous binder, Bio-oil, Biochar, Modification, Pine cone

Öz

Bu çalışmada, çam kozalaklarının pirolizinden elde edilen biyoçar ve biyo-yağın bitümlü bağlayıcı üzerindeki etkisi incelenmiştir. Bitümlü bağlayıcı, %5, 10 ve 15 oranlarında biyoçar ve %2, 4 ve 6 oranlarında biyoyağ kullanılarak modifiye edilmiştir. Saf ve modifiye bitümlü bağlayıcıların fiziksel ve reolojik özellikleri penetrasyon, yumuşama noktası, dönel viskozimetre (RV) ve dinamik kesme reometresi (DSR) testleri ile incelenmiştir. Deneylerden elde edilen veriler kullanılarak bağlayıcıların sıcaklık hassasiyetleri ve tekerlek izi dirençleri değerlendirilmiştir. Çam kozalaklarından elde edilen biyoçar ve biyoyağ gibi pirolitik ürünlerin bitümlü bağlayıcılarda katkı maddesi olarak kullanımının, bitümlü bağlayıcının sıcaklık hassasiyetini azaltabileceği ve tekerlek izine karşı direncini arttırabileceği belirlenmiştir.

Anahtar Kelimeler: Bitümlü bağlayıcı, Biyo-yağ, Biyoçar, Modifikasyon, Çam kozalağı

1 Introduction

Increasing traffic volume and negative environmental conditions cause asphalt pavements to deteriorate in a shorter time than expected [1,2]. Conventional bituminous binders are insufficient to overcome this deterioration in pavements [3]. Thus, additives such as polymers are used in asphalt mixtures to prevent deterioration and extend the service life [4]. Styrene-butadiene-styrene (SBS), polyethylene (PE), polypropylene (PP), ethylene-butyl acrylate (EBA), reactive ethylene terpolymers (RET), and ethylene-vinyl acetate (EVA) are among the polymers frequently used [5]. The high cost of polymers poses a significant challenge to their application as additives in bituminous binders. For this reason, extensive research is currently being carried out to investigate and develop alternative additives that can effectively replace polymers in bituminous binders. An important strategy to promote sustainability in the future is the use of biomass in versatile asphalt construction, taking into account both ecological and economic aspects [6].

Biomass refers to organic matter, such as plants, wood, agricultural waste, and other biological materials, that can be used as a source of energy. Various methods can transform biomass into different energy forms. The most common methods for converting biomass into energy are combustion, gasification, and anaerobic digestion [7]. Pyrolysis is another method of converting biomass into energy. In the pyrolysis method, biomass is heated in the absence of oxygen to produce biochar, a solid carbon-rich material, and bio-oil, a liquid mixture of organic compounds [8]. Biochar is a carbon-rich material obtained from the pyrolysis process. The physical, chemical, and structural properties of biochar are influenced by many factors such as biomass type, particle size, and pyrolysis temperature [9]. Pyrolytic oil, also known as bio-oil and obtained from pyrolysis of biomass, is a dark-brown organic oil [10,11]. The fact that biochar obtained from pyrolysis of biomass, which is a renewable and sustainable resource, is rich in carbon and bio-oil has similar physicochemical properties to bituminous binder has increased the interest in these materials [12-14].

Recently, bio-oil and biochar obtained from various biomasses have been used in the bituminous binders and mixtures as additives. Yang et al. tried to determine the properties of the asphalt mixture by adding three different bio-oils obtained from wood wastes by fast pyrolysis method

* Sorumlu yazar / Corresponding author, e-posta / e-mail: ibrahim.aslan@bozok.edu.tr (İ. Aslan)
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to the bituminous binder of PG (Performance Grade) 58-28 class at the rate of 0, 5, 10 %. As a result of their study, they stated that bio-oil can significantly improve the fatigue performance of mixtures, but it has no significant effect on rutting performance and dynamic modulus. They stated that the performance of the mixtures prepared with polymer-modified bio-oil was the best. As a result of the statistical study, they stated that the type and ratio of bio-oil in the mixture did not significantly affect the modulus of elasticity and rutting performance of the mixture, while it significantly increased fatigue performance. They also stated that bio-oil obtained from waste wood can be a good additive material for modification if used at a ratio of less than 10 wt% [15]. Zhou et al. also utilized bio-oil and biochar derived from waste wood and pig manure as biomass materials for enhancing bituminous binders. Their experimental findings revealed that the addition of biochar had a substantial impact on various fundamental properties of the bituminous binder, such as penetration, softening point, ductility, viscosity, and complex modulus. An important discovery was that bio-oil could be employed as a viable substitute for bituminous binder, either partially or entirely [16]. Pine cones are a popular kind of biomass waste that is an abundant and widely accessible resource. They have the potential to be a source of carbon. Pine cones comprise cellulose, lignin, and resins, all of which include a wide range of organic chemicals [17-19]. The reproductive structures of the pine tree are contained inside the pine cone, which is an organ of the pine tree. Each year, a significant amount of pine cones are created all over the globe as a by-product of agricultural production. Pines are classified as one of the most economically significant tree species since they are highly appreciated all over the globe for their timber and wood pulp [20].

In this study, biochar and bio-oil obtained from pyrolysis of pine cones, which have not been used in the literature before, were used as bituminous binder additives. In the study, the viscosity, softening point, penetration and temperature susceptibility of the bituminous binder were investigated by adding biochar and bio-oil obtained from the pyrolysis of pine cones to the bituminous binder in at least 3 different ratios. It is aimed to develop a bituminous binder additive material that will improve the properties of flexible road pavements and to eliminate the deficiency in the literature.

2 Material and method

2.1 Material

The natural bituminous binder, specified as B50/70 penetration grade for this study, was sourced from the TUPRAS Kırıkkale petroleum refinery. Details of the binder's properties are presented in Table 1.

Pine cones were used as a source of biomass in this study. Pine cones that were classified as garbage were gathered from the "Yozgat Çamlık" national park. The pine cones were ground to sizes ranging from 1 to 2.5 cm and subjected to a pyrolysis process. Figure 1 illustrates the initial state of the pine cone before pyrolysis, as well as the products acquired after pyrolysis.

Table 1. Properties of the natural bituminous binder

Properties	Standard	B 50/70
Penetration (0.1 mm)	AASHTO T49	51.2
Softening Point (°C)	AASHTO T53	48
Penetration Index (PI)		-1.66
Specific Gravity	AASHTO T228	1.03
Viscosity (cP, 135 °C)	AASHTO TP48	437.5
Viscosity (cP, 165 °C)	AASHTO TP48	100

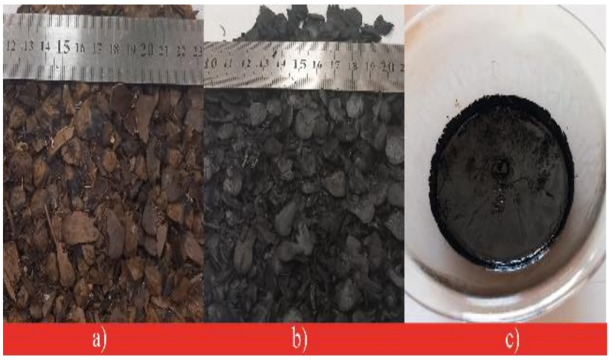

Figure 1. a) Pine cone pieces before pyrolysis, b) biochar, c) bio-oil

2.2 Method

Thermal degradation processes vary between 200-1000 °C [21]. Studies on the efficiency of biochar have shown that 300 °C temperature provides higher efficiency than higher temperatures [22]. The pyrolysis procedures were conducted at a temperature of 300 °C. The biochars produced through the pyrolysis process were passed through using a sieve with a 0.075 mm aperture and prepared for use as additives in bituminous binders. In the studies carried out with biochar, it was determined that the additive rate varied between 2-20% and the optimum rate was below 10% [23]. In this study, the bituminous binder was supplemented with biochar additions at 5, 10, and 15 percent. The bio-oils derived from the pyrolysis process were fractionated using a distillation apparatus. Following the temperature of 360 °C, the most substantial fractions were employed as additives for bituminous binders. It was stated that different techniques may be needed for bio-oil utilisation rates of 6% and above [24]. Therefore, the bituminous binder was supplemented with bio-oil additives at concentrations of 2, 4, and 6 weight percent. The modification procedure was successfully executed within a time period of 30 minutes, at a temperature of 150 °C, and with a rotation speed of 1000 rpm.

Conventional binder tests were conducted to determine the penetration and softening point of the natural and modified bituminous binders. Additionally, performance tests involved the use of a rotational viscometer (RV) and dynamic shear rheometer (DSR) to assess the properties of the binders. Penetration tests of the binders were carried out following the AASHTO T49 test standard, and softening point tests were carried out following the accordance with the AASHTO T53 test standard. Utilizing both penetration and softening point data, the penetration indices (PI) of binders were calculated following Equation (1)[4]. The penetration index provides information on the thermal susceptibility of bituminous binders, with this number being inversely related to temperature susceptibility. The susceptibility of bituminous binders to temperature rises as their PI values fall [25].

$$PI = \frac{1952 - 500log(Pen) - 20SP}{50log(Pen) - SP - 120} \quad (1)$$

In Equation (1), the variable SP represents the softening point of bituminous binders, whereas the variable PEN represents the penetration value. The Penetration-viscosity numbers (PVN) were determined by utilizing the penetration and viscosity measurements of the binders. The PVN, suggested by McLeod [26], is an additional metric that enables the assessment of temperature susceptibility and the capacity to avoid the formation of cracks in bituminous binders at low temperatures. A lower PVN value indicates increased temperature susceptibility of the bituminous binder, similar to PI. The PVN values of bituminous binders are calculated using Equation (2) [4, 27, 28].

$$PVN = -1.5\frac{4.258 - 0.7967logP25 - logV}{0.795 - 0.1858logP25} \quad (2)$$

In the given equation, P25 represents the penetration value of the binder at a temperature of 25 °C. V, on the other hand, represents the viscosity value of the binder at a temperature of 135 °C, measured in centipoise (cP).

Another suitable method to evaluate the temperature susceptibility of bituminous binders is the viscosity-temperature susceptibility (VTS) method [29]. This method utilizes the variation in viscosity of bituminous binders between two different temperatures. The significant variation in viscosity with temperature demonstrates the bituminous binder's susceptibility to changes in temperature. A greater VTS value indicates increased temperature susceptibility of the bituminous binder. The calculation of VTS values is carried out with Equation (3) [4, 30].

$$VTS = \frac{\log(\log(V1) - \log(\log(V2)}{\log(T2) - \log(T1)} \quad (3)$$

The equation involves the temperatures T1 and T2, which are used to determine the viscosity values. Similarly, V1 and V2 represent the viscosity values at these respective temperatures.

The fracture temperatures of the binders were computed using Equation (4). The estimated temperatures at which bituminous binders fracture are connected with their penetration and penetration index (PI). Equation (4) is proposed as a method to determine the minimum service temperature (T_{design}) for the efficient functioning of bituminous binders [31-33].

$$\begin{aligned} Tdesign &= 32.9 - 30.9 \text{ logPen} \\ &+(3.7 - 4.67 \text{ logPen}) \text{ PI} \end{aligned} \quad (4)$$

Equation (4) defines the "Pen" as binder's penetration value, whereas PI represents the penetration index. The estimated fracture temperature is defined as 10 °C below the minimum service temperature [32].

Dynamic shear rheometer (DSR) tests were conducted to assess the performance characteristics of the binders. The Dynamic Shear Rheometer is a device utilized to examine the viscoelastic characteristics of bituminous binder and to assess their resistance to rutting and cracking. The DSR test quantifies the complex modulus (G*) and phase angle (δ) of the asphalt binder at various temperatures and frequencies, indicating its characteristics as a solid with elasticity at low temperatures and a liquid with viscosity at high temperatures [34]. A bituminous binder with a high complex shear modulus (G*) value offers greater rigidity and resistance to deformations, while a bituminous binder with a low phase angle (δ) allows for more deformation recovery due to its higher proportion of elastic components [35]. DSR tests were conducted on both natural and modified bituminous binders in accordance with the AASHTO T315 standard.

In this study, six different groups of modified bituminous binders were produced as a result of the modification procedure. 7th group is a natural bituminous binder. Each conventional test applied on natural and modified bituminous binder groups was repeated 3 times. Figure 2 displays the experimental program of the investigation.

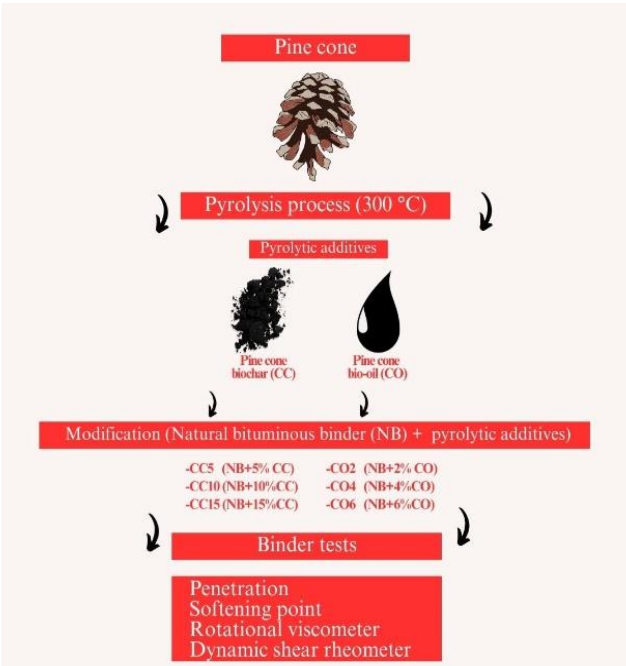

Figure 2. Experimental program

3 Results and discussion

Within the scope of the investigation, the abbreviation NB stands for natural bituminous binder, CC stands for cone biochar addition, and CO stands for cone bio-oil additive. It is the additive content of the modification that is represented by the number that is next to the names of the additives.

The penetration values of natural and modified bituminous binders are presented in Figure 3.

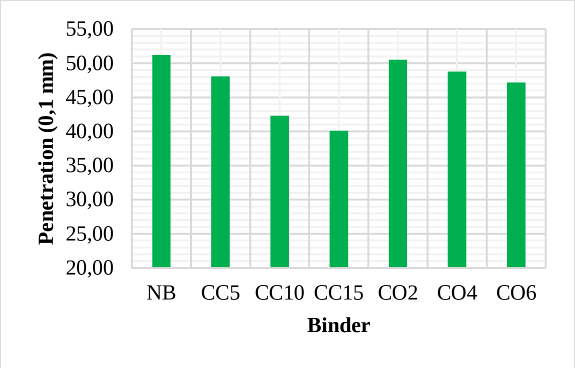

Figure 3. Penetration test results

Figure 3 demonstrates that adding any additives decreased the penetration value of the natural bituminous binder, thus increasing its stiffness. The CC-type provided the most significant contribution to the penetration values. Adding CC additive at weight percentages of 5, 10, and 15 resulted in reductions of 6.1%, 17.4%, and 21.7% in the penetration values of the natural bituminous binder, respectively. The inclusion of CO-type additives reduced the penetration value of the natural bituminous binder by 1.4%, 4.7%, and 7.8% at additive rates of 2%, 4%, and 6%, respectively. It was found that the biochar additive had a greater effect on the change in penetration results than the bio-oil additive.

Figure 4 displays the softening point values of natural and modified bituminous binders.

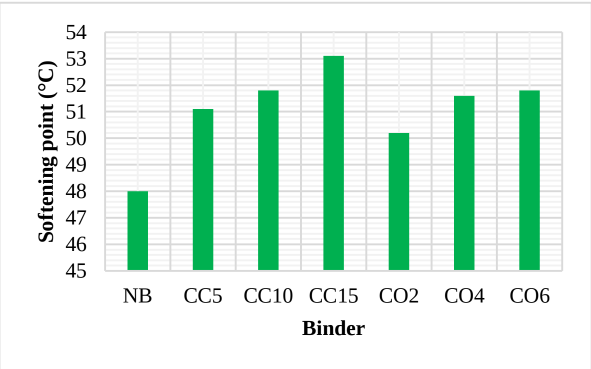

Figure 4. Softening point test results

Upon examining the softening point temperatures of the binders, it is evident that the values vary in parallel to the change in penetration values. The binders containing CC additives exhibited the most significant increase in softening point values. The results demonstrated that adding CC additives at 5, 10, and 15 wt% resulted in a respective rise of 6.5%, 7.9%, and 10.6% in the softening point values of the natural bituminous binder.

The viscosity values of natural and modified bituminous binders at 135 °C and 165 °C temperatures are presented in Figure 5.

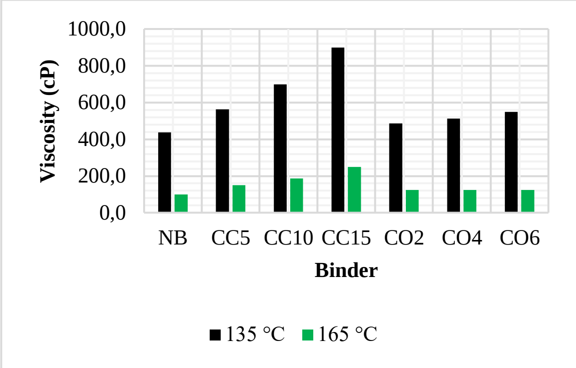

Figure 5. Rotational viscometer test results

According to the SUPERPAVE bituminous binder specification, binders must have no more than a viscosity of 3000 cP at a temperature of 135 °C. Figure 5 demonstrates that the viscosity values of the binders are below 3000 cP at a temperature of 135 °C. The impact of biochar additives on the viscosity change of natural bituminous binder is more significant than that of bio-oil additives. The addition of biochar to bituminous binders resulted in an increase in viscosity at both temperatures. However, binders with varying amounts of bio-oil had the same viscosity value at 165 °C.

The temperature susceptibility of the binders was assessed using the PI, PVN, and VTS values. PI values based on penetration and softening point values are given in Figure 6.

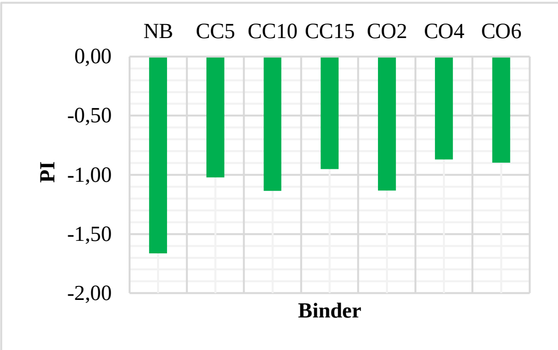

Figure 6. PI values of binders

Upon examining the PI values of the binders, it is evident that adding additives increases the PI values of the natural bituminous binder. This effect serves to decrease the binder's susceptibility to changes in temperature. The study revealed that the addition of the CO additive had the most significant impact on the temperature susceptibility of the natural bituminous binder. This effect is obtained by using a 4% additive component. The CO addition with a 4% content enhanced the PI value of the natural binder by 47%.

The PVN values, which assess the temperature susceptibility of the binders, were determined by analyzing the penetration and viscosity values of the binders at a temperature of 135 °C. These results are illustrated in Figure 7.

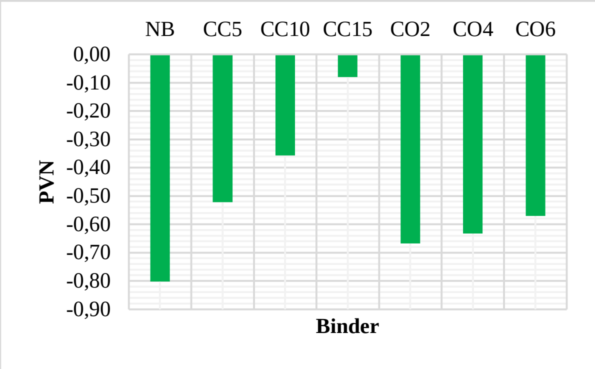

Figure 7. PVN values of binders

High PVN values indicate a reduced level of temperature susceptibility, similar to the PI method. Upon analyzing the PVN values of the binders, it becomes evident that both types of additions tend to reduce the temperature susceptibility of the natural bituminous binder. The PVN values positively correlate with the rising amount of additive material. CC additive demonstrates greater efficacy than CO additive in the context of the PVN approach. Adding a 15% percentage of CC addition resulted in an essential rise in the PVN value of the natural bituminous binder, increasing it from -0.8 to -0.08.

The VTS values, calculated based on the viscosity measurements of the binders at temperatures of 135 °C and 165 °C, are displayed in Figure 8.

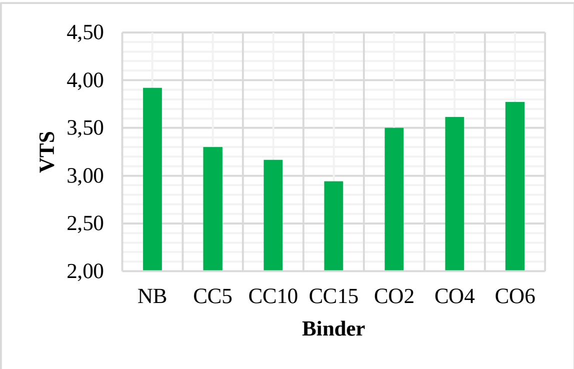

Figure 8. VTS values of binders

Upon examination of the VTS values used to assess the temperature susceptibility of the binders, it is shown that all modified bituminous binders exhibit lower values than the natural bituminous binder. The reduced VTS values of the modified bituminous binders indicate their temperature susceptibility is lower than that of the natural bituminous binder. The CC additive was the most beneficial in terms of VTS values. The progressive increase of the additive component in biochar leads to a consistent reduction in VTS values. However, an increased amount of additive in the bio-oil leads to an increase in VTS values and thus results in greater temperature susceptibility. However, although it contains 6% bio-oil, the VTS value is still lower than that of the natural bituminous binder.

The estimated fracture temperatures were determined based on the minimum service temperature values calculated according to the penetration and penetration index values. Figure 9 represents the estimated fracture temperature of the binders to be used in the design.

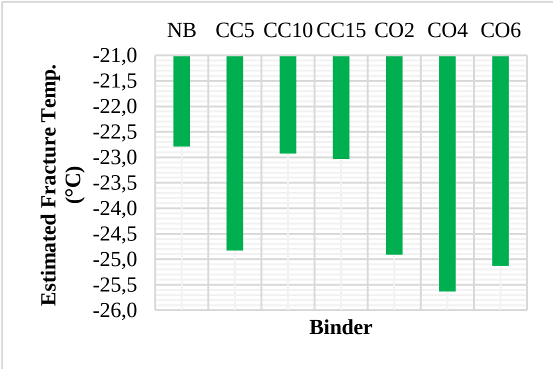

Figure 9. The minimum service temperature of the binders

It can be observed that the use of biochar in 5% concentration reduces fracture temperature compared to its use in 10% and 15% ratios. Using bio-oil gives better results than biochar for fracture temperatures. Using 4% bio-oil gives the lowest fracture temperature value.

(G*) and (δ) parameters of the binders were determined due to DSR tests on natural and modified bituminous binders. The G*/sinδ values used to determine the rutting resistance of the binders are presented in Figure 10.

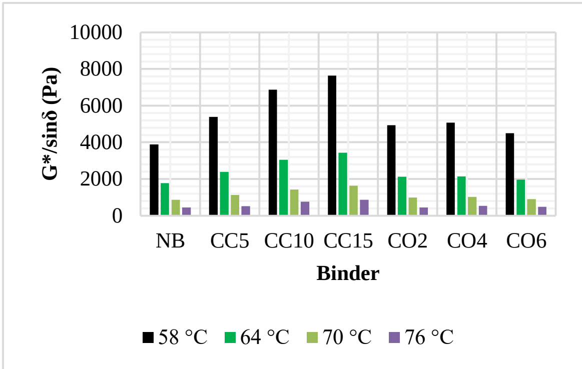

Figure 10. DSR test results

Upon analysis of the G*/sinδ data, which represents the rutting parameter of the binders, increasing the amount of biochar additives leads to an increase in these values. According to the SUPERPAVE binder standard, unaged binders must have G*/sinδ values above 1000 Pa. The criteria are met at a temperature of 64 °C for natural bituminous binder and at 70 °C for binders having additives with CC contents. The CC-type additive was the most efficient in terms of its ability to resist rutting. Utilizing the bio-oil additive significantly improved the rutting resistance of the pure bituminous binder but did not cause a significant change in the high-temperature performance grade.

4 Conclusions

The following results were obtained in this study where biochar and bio-oil obtained from the pyrolysis of pine cones were used as bituminous binder additives.

- Based on tests of the physical properties of bituminous binders, adding biochar and bio-oils as bituminous binder modifiers increased the softening point and decreased the penetration values.
- The results of the softening point and penetration tests indicate that both types of additives and all contents reduced the temperature susceptibility of the natural bituminous binder. Based on the VTS and PVN results, it can be concluded that adding biochar is more efficient than adding bio-oil in terms of the susceptibility to the temperature of the binder. Regarding PI, both additives have favorable results compared to natural bituminous binder in all ratios. The estimated fracture temperatures of modified bituminous binders containing bio-oil and biochar were found to be lower than those of natural bituminous binder. Thus, it was observed that the low temperature performance of modified bituminous binders was better than that of natural bituminous binder.
- The DSR test results indicate that the addition of bio-oil additives has a positive effect on rutting resistance. However, it did not improve the high-temperature performance grade of the natural bituminous binder. The presence of biochar as a component enhanced resistance to deformation of the natural bituminous binder. In addition, the biochar additive increased the high-temperature performance grade of the bituminous binder.

Based on the data collected in this study, combining biochar and bio-oil additives derived from different biomasses in future research can yield favorable outcomes in terms of reducing low temperatures, increasing high temperatures, and minimizing permanent deformations. It is also essential to investigate the effectiveness of bituminous mixtures containing these additives by performance tests such as rutting, fatigue cracking and low-temperature cracking tests.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Similarity rate (iThenticate): 16%

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