From biowaste to BioPave: Biological pathways for sequestration of anthropogenic CO_2 and enhancing durability of roadway infrastructures

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ABSTRACT

Biomass-derived bio-oils are emerging as sustainable, low-carbon alternatives for construction materials, particularly in innovative pavement applications, 'BioPave'. This study evaluates bio-oils from various sources, including algae and wastewater biomass, revealing variations in carbon, nitrogen, and sulfur contents, along with viscosity. We focused on their application in outdoor construction, assessing their resistance to thermal and solar radiation, and moisture. The study also examines their interaction with siliceous surfaces and their influence on asphalt adhesion in BioPave systems under moisture conditions. Laboratory experiments and computational modeling demonstrated molecular composition significantly influenced bio-oils' responses to thermal and UV exposure. Bio-oils rich in polar groups showed hardening upon thermal treatment, while those with higher concentrations of saturated aliphatics remained more stable. Furthermore, our findings highlight the significance of dosage control in maximizing beneficial effects of bio-oils in intermolecular interactions at bitumen-aggregate interface in BioPave applications. These findings offer insights into the potential of bio-oils in sustainable construction and the need for dosage control to optimize pavement performance.

1. Introduction

In the United States, asphalt pavements are a major component of a vast roadway network that supports commerce, transportation, and daily life for millions. The consistent demand for asphalt in the U.S. reflects not only the need for new infrastructure projects but also the maintenance and rehabilitation of existing roads. Two primary challenges for asphalt pavements are moisture exposure and thermal fluctuations: moisture exposure can lead to a weakening of asphalt's binding properties, resulting in premature pavement failure; thermal fluctuations can cause asphalt to crack and degrade over time (Kakar et al., 2015; Lu and Isacsson, 2002; Qin et al., 2014). By modifying asphalt formulations with bio-modifiers, it is possible to enhance asphalt's resistance to these environmental stressors (Pahlavan et al., 2021; Pahlavan et al., 2023; Yang et al., 2023). These bio-modifiers can strengthen the adhesive and cohesive bonds within pavement, making it more resilient against water intrusion and temperature-induced damage. As the need for sustainable and long-lasting roadways grows, leveraging bio-based modifiers to enhance the performance of asphalt pavements offers a promising approach to address these infrastructure challenges.

Carbon-based materials, including bio-oils, play a significant role in the construction industry, particularly in the modification of materials such as asphalt. However, a critical concern is the CO_2 emissions associated with the entire life cycle of carbon-modified constructions. Addressing this concern is the strategy to design and champion carbon-negative additives for modifying asphalt pavement. Using asphalt modifiers derived from renewable resources, as opposed to traditional fossil-fuel non-renewable resources, leads the way for a more sustainable approach to enhancing asphalt's performance. The growing emphasis on carbon-neutral construction, combined with the successful prior implementations of carbonaceous materials in improving asphalt's attributes, lends credence to the viability of integrating a bio-oil as an essential asphalt additive (Girimath and Singh, 2019; Zahoor et al., 2021; Su et al., 2018; Flávia Justino Uchoa et al., 2021; X. Zhang et al., 2020; Hu and Gholizadeh, 2020). Notably, bio-oils derived from

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biomass are rich in carbon content: up to 77 % of a bio-oil's composition is carbon (T. Zhou et al., 2021). By harnessing these carbon-rich bio-oils, which not only have lower production costs (Snowden-Swan et al., 2022; Zhu et al., 2022) but also minimal or even negative carbon footprints, (Cai et al., 2022) the bituminous construction industry can transform pavements into carbon sinks. Such innovative practices can effectively store and sequester carbon within the structure, moving toward achieving carbon neutrality in construction.

As non-renewable sources of asphalt binder become depleted and modern refining methods yield less binder, there is increasing demand for renewable sources of asphalt binder. Recent research has shown a promising direction in this regard, promoting the use of bio-oils derived from biomass (X. Zhang et al., 2020; Wang et al., 2020; X. Zhou et al., 2021; Lv et al., 2021; Ding et al., 2021). These bio-oils, sourced from organic materials, offer an eco-friendly, sustainable solution with the potential to revolutionize the asphalt industry. Bio-oils not only address the pressing issue of depleting traditional sources of asphalt binder but also align with global efforts to reduce carbon footprints and embrace greener construction materials. In recent research, a variety of biomass sources have been explored for their potential in bio-oil production: woody biomass (such as pine); animal waste; agricultural residues (such as rice husks); algae; and waste cooking oil (Pahlavan et al., 2022; Yang et al., 2014; Fini et al., 2011; X. Zhang et al., 2020; Sun et al., 2016; Sun et al., 2016; Ahmed and Hossain, 2020; R. Zhang et al., 2020). In the context of building a circular bioeconomy, biomass emerges as a pivotal resource, offering the potential to maximize resource value indefinitely while minimizing unrecoverable waste. The comprehensive understanding and integration of sustainable biomass production, spanning from product design to waste management, is essential for realizing the circular economy's ideals (Sherwood, 2020).

Recent studies conducted by our research group and other researchers have highlighted the potential of bio-oils as rejuvenators for oxidatively aged asphalt binder (Pahlavan et al., 2019; Rajib et al., 2020; Pahlavan et al., 2020; Ye et al., 2023; Zahoor et al., 2021; Wang et al., 2023; Jiang et al., 2023). These investigations pointed out that bio-oils not only compensate for the compounds lost from asphalt binder during the process of oxidative aging but also effectively disintegrate the large molecular agglomerates that intensify in asphalt binder with aging. Moreover, the molecular composition of the bio-oil was found to have a profound influence on its stability in the asphalt mixture. This, in turn, directly impacts the durability and longevity of the asphalt pavement. By addressing these multifaceted challenges, the studies underscored the capability of bio-oils to restore both the rheological and the morphological properties of asphalt binder, ensuring its sustained physical performance despite the adversities of oxidative aging.

Biowaste feedstocks have diverse biochemical profiles based on their origin and composition. These biochemical intricacies play a crucial role in shaping the behavior of various components during processes such as hydrothermal liquefaction (Li et al., 2014). They not only impact the efficiency and conditions of the hydrothermal process but also influence its overall yield and the resulting chemical composition of the products (Cheng et al., 2018; Chen et al., 2014). Consequently, each resulting bio-oil has unique molecular characteristics that shape its efficacy as a modifier in various applications (Pahlavan et al., 2019). A compelling illustration of this is evident from a prior study undertaken by our team (Pahlavan et al., 2020). When evaluating the performance of bio-oils obtained through hydrothermal liquefaction, it was discovered that a balanced feedstock composed of swine manure and algae yielded a superior product. Specifically, this combined bio-oil outperformed those derived solely from either algae or manure in enhancing asphalt's resistance to moisture damage. This superior performance can be attributed to the synergistic blend of lipid-rich swine manure with protein-abundant algae. The resulting molecular composition of this bio-oil, named "Swilgae," displayed both decreased polarizability and increased adsorption energy per siliceous surface unit area compared to bio-oils derived from the individual feedstocks. Swilgae molecules compete with water molecules for attachment to a hydroxylated silica surface. The outcome is the formation of a robust bridge by Swilgae molecules, bridging bitumen and siliceous substrates. This results in augmented adhesive forces, which ultimately translate to enhanced durability in the bituminous composites commonly used in pavement and roofing applications. In a comparative study, the molecular components in a bio-oil derived from the co-liquefaction of swine manure and algae exhibited lower polarizability and superior resistance to moisture (Pahlavan et al., 2021). In contrast, the components found in waste vegetable oil showed heightened polarizability and reduced resistance to moisture (Mousavi et al., 2020).

Building on the insights gleaned from prior research, there is a keen interest in harnessing the advantages of combining diverse feedstocks. The goal is to produce bio-oils that act as high-efficiency additives for asphalt binder and other materials. This research investigates several unique sources of algal biowaste across broad sources, targeting cost-advantaged sources of biomass. That is, feedstock sources which are considered a biowaste or by-product with no value to the producer and can therefore be sold or transferred to a processor for nominal costs. By blending distinct feedstocks, it is anticipated that the resulting bio-oils will demonstrate enhanced thermal stability, a crucial characteristic for withstanding temperature fluctuations and prolonging the lifespan of the material. Additionally, by optimizing the combination of feedstocks, there is the potential to significantly reduce the susceptibility to moisture, ensuring that the bio-modified asphalt binder remains resilient against moisture-induced damage. It is important to clarify that in this study, when we refer to 'blending feedstocks,' we mean the process of combining different raw materials before bio-oil production. This is distinct from 'blending bio-oils,' which involves mixing finished bio-oils from various sources. Our research specifically focuses on the former, exploring the synergistic effects of different feedstocks on bio-oil production, rather than the post-production blending of bio-oils. While our research investigates the synergistic effects of blending diverse feedstocks, it also critically examines the performance of singular, non-blended feedstocks to identify cases where the unique properties of a single source might independently produce bio-oils with advantageous characteristics, thus justifying the selective approach to blending in our study. This dual approach, targeting both thermal stability and moisture resistance, aims to revolutionize the formulation of bituminous composites, setting new benchmarks for durability and performance.

To comprehensively investigate the suitability of bio-oils derived from diverse biomass sources for construction applications, this study examines their behavior under various conditions. We assess the physical properties of these bio-oils, such as their solidification characteristics and hardness upon cooling, and their reactivity to UV exposure. Utilizing Attenuated Total Reflectance Fourier-Transform Infrared Spectroscopy (ATR-FTIR), we analyze the chemical composition and molecular responses of bio-oils from various biomass sources, assessing their reactivity under heat and UV exposure to evaluate their performance, stability, and moisture interactions for construction material applications. Additionally, we explore their moisture absorption capacity and its implications for moisture resistance. The Moisture-Induced Shear-Thinning Index (MISTI) Test, a recently developed test, evaluates the susceptibility of the bitumen-aggregate interface to moisture damage, assessing the efficacy of each bio-oil as a bitumen modifier. Complementing these experimental approaches, we delve into the molecular properties of the bio-oils using Density Functional Theory (DFT). This involves assessing the polarizability of the predominant compounds in the bio-oils, offering insights into their thermal stability and variability under thermal conditions. By correlating the average polarizability values and polarizability ranges with the bio-oils' behavior, we aim to deduce the thermal and oxidative stabilities of these oils. This multi-faceted approach, combining practical tests and computational analysis, seeks to advance our understanding of bio-oils as sustainable alternatives in construction materials, particularly in paving applications.

2. Materials and methods

2.1. Bio-oil production

This study is a comprehensive exploration of diverse biomass categories as feedstocks for bio-oil production, highlighting the versatility and sustainability of using a variety of biomass feedstocks in the quest for eco-friendly alternatives in construction applications. The investigated biowaste sources encompassed a spectrum of materials, including harvested algal bloom materials, purpose-grown microalgae, and wastewater-sourced biomass. The following list summarizes the biomass sources and their associated abbreviations given to the bio-oils used in this study.

Algae-1: Lake-harvest algal biomass. The algae were provided by the Engineer Research and Development Center of the US Army Corp of Engineers. The algae were harvested at the Saddle Creek spillway in Polk county, FL using dissolved air flotation.

Algae-2: Lake-harvested algal biomass blended with Engineered BioSlurry (EBS®). The algae were provided by AECOM from Lake Jesup in Seminole county, FL. EBS® was provided by Waste Management. The algal biomass was blended with EBS to facilitate HTL processing by increasing the net amount of lipids and reduced the net amount of ash in the feedstock. The mass ratio of algae and EBS was 4:1.

Algae-3: Lake-harvested algal biomass blended with wood powder. The algae were provided by AECOM from their algae harvester located at William H. Harsha Lake in Clermont county, OH. The algae were harvested using AECOM's Hydronucleation Flotation Technology. The algae were blended with wood powder on a 1:4 algae:wood ratio after harvesting to facilitate dewatering.

Algae-4: Wild-type seaweeds, mostly *Ulva* sp., collect from the shore near Sequim, WA.

Algae-5: Post-extraction *Haematococcus pluvialis* was provided by Cyanotech Corporation (Kailua-Kona, HI). The biomass was provided water-free.

Algae-6: Wastewater-grown algal biomass provided by Gross-Wen Technologies (Slater, IA). The consortia of algae were grown on a biofilm submerged in primary effluent using a Revolving Algal Biofilm (RAB™) system.

WWS: Primary and secondary wastewater sludges from the Great Lakes Water Authority (Detroit, MI). The mass ratio of primary and secondary sludges was 43:57.

We used hydrothermal liquefaction (HTL) to produce bio-oil from each biowaste under controlled conditions. Each feedstock was processed using a continuous-flow system for HTL. Processing conditions are shown in Table 1. During HTL in the continuous-flow system, solids were removed with an inline filter and the resulting bio-oil and aqueous phase products were collected after pressure letdown to ambient pressure. The bio-oil and aqueous-products were transferred to a separatory funnel and the aqueous phase was decanted. The collected bio-oil was subsequently sealed and stored at room temperature conditions (between 20 and 22 °C) prior to additional testing. Details of the HTL process and equipment design can be found in our previous publication (Marrone et al., 2018).

Table 1
Key processing details for HTL.

Sample	% solids in the slurry	Reactor temperature (°C)	Pump pressure (psig)	Volume at reaction temperature (mL)	LHSV (L/L/h)
Algae-1	17	330	2900	1050	1.9
Algae-2	12	320	2800	500	10
Algae-3	14	330	2800	550	4.3
Algae-4	18	330	2900	550	3.6
Algae-5	20	340	2900	1050	3.8
Algae-6	16	340	2900	1150	1.7
WWS	18	320	2800	1050	3.8

2.2. Preparation of samples

This study used bitumen with a performance grade (PG) of 70–10. Glass beads (100 μm), used for the MISTI test (explained in detail on page 8), were supplied by Gesswein (Bridgeport, CT). Additionally, bio-oils were produced and intended to be mixed into bitumen separately to serve as modifying agents. Bitumen modification involved adding the bio-oils separately to the bitumen and mixing at a temperature of 150 °C for 5 min using a stainless-steel lab spoon. To prepare samples of bitumen modified by a bio-oil, two dosages of each bio-oil (3 % and 6 % by bitumen weight) were incorporated separately into bitumen. Subsequently, glass beads were introduced to the modified bitumens at a 2:1 ratio (by weight).

2.3. Infrared spectroscopy with heat and uv exposure

Attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) was performed using a Thermo Scientific Nicolet iS20 spectrometer equipped with a Pike Technologies GladiATR Illuminate accessory module that enables measurement of the sample at elevated temperature (up to 210 °C) or under light illumination through the diamond ATR crystal. For measurements under heat or UV exposure, the stage was pre-heated to 120 °C and the illumination from a 365 nm UV LED lamp was set to an intensity of 14 mW/cm^2, delivered to the accessory through a liquid light guide and measured at the ATR crystal. For context, the UV intensity (280–400 nm) at midday in summer in Tempe, AZ, was measured with a handheld UV $A + B$ light meter to be about 8 mW/cm^2.

A razor blade and 0.17-mm-thick glass coverslip spacers were used to doctor blade coat a thin film of bio-oil onto the ATR crystal for measurement. The cover of a glass petri dish was placed over the sample during measurement to minimize odors. Vapors condensed as a visible fog on the dish, and these condensates could be collected with a cotton swab and applied to the ATR crystal to be measured independently. Single spectra were acquired with 4 cm^{-1} resolution, zero baselined by single-value subtraction (absorption at 1824 cm^{-1}) and normalized to the peak at 1453 cm^{-1} for plotting and qualitative comparison. Time-series spectra were collected with 16 cm^{-1} resolution once per minute for one hour and were normalized to the integrated absorption intensity of the fingerprint region (1860–450 cm^{-1}).

For preliminary measurements of mass loss, about 1 g of each bio-oil sample was put in a shallow watch glass dish, and the dish was placed in a vacuum oven. The mass of each sample was measured after 18 h at 120 °C and 25 inHg vacuum-gauge pressure.

2.4. Moisture-induced shear-thinning index (MISTI) test

The moisture-induced shear-thinning index (MISTI) test was recently developed to quantify the susceptibility of a bitumen-aggregate interface to moisture damage. The MISTI test was used in this study to examine the efficacy of each bio-oil as a modifier for bitumen. To do so, a shear-rate ramp test was performed on a mixture of bio-modified bitumen and glass beads using a dynamic shear rheometer (Anton Paar MCR 302 DSR) with an 8-mm spindle. A mixture containing a 2:1 ratio of bitumen and glass beads was placed in a silicon mold to form an 8-mm disk-shaped specimen. Each specimen was then demolded and placed in a parallel-plate test setup of a DSR to be tested. A ramping shear rate (0.1–100 1/s) was applied on the specimen, and the viscosity value was measured at each shear rate. The testing temperature was

adjusted so that the initial viscosity was close to 1000 Pa.s. A plot of viscosity versus shear rate was then used for analysis, as shown in Fig. 1. The behavior of shear thinning is linked to the intermolecular interaction at the interface of bitumen and silica; a higher shear-thinning slope indicates stronger interaction between bitumen and silica (Aldagari et al., 2022; Faisal Kabir et al., 2021). For each bitumen, two samples were tested while remaining unconditioned, and two other samples were conditioned in distilled water at 60 °C for 24 h before testing. After that, for each bitumen, the MISTI value was determined using Eq. (1), based on the shear-thinning slopes before and after water conditioning. The change in shear-thinning slope after water conditioning is closely related to the effect of water at the interface between the bitumen and the glass beads. A MISTI value closer to 1 indicates better resistance to moisture damage (Aldagari et al., 2022; Faisal Kabir et al., 2021; Rajib et al., 2021).

$$MISTI = \frac{\text{Average (shear} - \text{thinning) slope of Dry Specimen}}{\text{Average (shear} - \text{thinning) slope of Wet Specimen}} \quad (1)$$

2.5. Computational methodology

Density Functional Theory (DFT) is a quantum mechanical modeling method used in physics and chemistry to investigate the electronic structure of many-body systems, particularly atoms, molecules, and the condensed phases (Sholl and Steckel, 2022). At the core of DFT is the principle that the ground-state properties of a many-electron system can be determined by a functional of the electron density alone. This theory simplifies the computational study of electronic properties by replacing the many-electron wave function with electron density as the primary variable. DFT has become a widely used method for electronic structure calculations in various fields due to its favorable balance between computational cost and accuracy.

Using DFT calculations, this part of the study sought to probe the molecular properties of the primary compounds present in bio-oils made through hydrothermal liquefaction and waste vegetable oil (WVO). WVO is characterized by a high content of acidic compounds, a property that has been extensively documented in the literature as influencing the moisture susceptibility of bituminous composites, especially in the presence of siliceous aggregates (Oldham et al., 2021). These acidic components are pivotal in assessing the moisture damage potential in bio-modified bitumen, with WVO serving as a critical benchmark in our study to represent a 'worst-case scenario' for moisture susceptibility. This approach allows for a nuanced comparison across different bio-oils, highlighting WVO's unique position in evaluating moisture resistance enhancements for bitumen without resorting to acid reduction processes such as transesterification. The incorporation of WVO, specifically a blend of soy, corn, and canola oils, mirrors the typical composition found in practical applications, providing a relevant and applicable foundation for our comparative analysis.

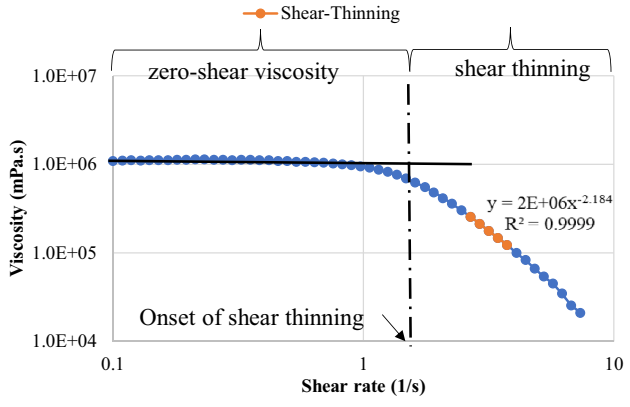

Fig. 1. Graph of viscosity versus shear rate: zero-shear viscosity, and shear-thinning zone.

Our primary focus was on the conceptual DFT descriptor, polarizability. Polarizability reflects a molecule's ability to distort its electron cloud when subjected to an external electric field; thus, polarizability can serve as an indirect measure of a molecule's reactivity and flexibility. High polarizability values often correlate with a molecule's heightened reactivity, heightened intermolecular interactions, and increased potential sensitivity to various environmental conditions, such as thermal exposure. In the context of bio-oils, discerning these molecular tendencies is paramount. By comparing the polarizability values of compounds across different bio-oils, we can anticipate their relative thermal stability. Essentially, the efficiency of using this descriptor lies in its ability to offer predictive insight into the performance of a bio-oil under specific conditions, without resorting to extensive experiments. The computational analyses were carried out with Gaussian 16 software, using a specific functional and basis set tailored for such molecular evaluations.

The reliability of conceptual DFT descriptors, especially polarizability, has been important to understanding the reactivity profiles of bio-oil compounds. In computational and quantum chemistry, polarizability is a measure of how the electronic cloud around a molecule or atom responds to an applied external electric field. More technically, it quantifies the extent to which a molecule can be distorted by such an external field. When an external electric field is applied, the positions of the electrons in a molecule can shift slightly, inducing a dipole moment (a separation of positive and negative charges) in the molecule. This induced dipole moment is proportional to the strength of the applied electric field, and the constant of proportionality is termed the polarizability. Mathematically, the induced dipole moment (μ_{ind}) and the applied electric field (E) are related as in Eq. (2):

$$\mu_{ind} = \alpha E \quad (2)$$

where α is the polarizability.

In computational practice, polarizability coefficients typically are determined through static frequencies. For this study, the components of frequency-dependent polarizability tensors (α_{xx}, α_{xy}, α_{yy}, α_{xz}, α_{yz}, and α_{zz}) were computed using frequency calculations with the Raman option (Freq = Raman) (Thanthiriwatte and Nalin de Silva, 2002).

In this part of the study, molecular structures were fully optimized using density functional theory methodology available in the Gaussian 16 software package (Frisch et al., 2016). The Becke's three-parameter hybrid exchange combined with the Lee–Yang–Parr correlation functional (B3LYP) (Lee et al., 1988; Becke, 1993) was our chosen functional, while 6-311G* served as the basis set. Following this, the linear polarizability, denoted as α, was meticulously calculated at the B3LYP/6–311G* level. This helped us assess the reactivity of compounds across seven distinct bio-oils. For clarity, the value of α is derived from its x, y, and z components using Eq. (3).

$$\langle \alpha \rangle = \frac{1}{3}\left[\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right] \quad (3)$$

3. Results and discussion

3.1. Mass loss and thermal hardening

Samples WWS and Algae-6 were initially unavailable in sufficient quantities for mass-loss testing. Table 2 shows the preliminary mass loss of five bio-oils in a vacuum oven. All samples except Algae-3 showed significant evaporative mass loss, although an unknown amount of that mass loss is water. For context, petroleum bitumen is expected to lose less than 1 % mass in a rolling thin-film oven test.

Qualitatively, most bio-oil samples hardened to a stiff and brittle solid upon cooling to room temperature after heating (see Supporting Information Figure S1). Algae-3 as received was already a stiff solid that softened with elevated temperature. It is notable that bio-oil samples

Table 2
Mass loss (%) of bio-oils after 18 h at 120 °C and 25 inHg vacuum-gauge pressure.

Sample	% mass loss
Algae-1	24.2
Algae-2	25.8
Algae-3	7.1
Algae-4	30.9
Algae-5	35.5
Algae-6	NA
WWS	NA

Algae-2 and WWS solidified into soft, ductile solids after thermal annealing. Algae-6 also annealed into a solid that was noticably softer than other samples but more brittle than Algae-2 and WWS.

3.2. FTIR spectra of bio-oils

Fig. 2 shows the FTIR spectra of the bio-oil samples as they were received, after 1 h at 120 °C, and after 1 h at 120 °C with 365 nm UV irradiation. Absorption bands of interest are highlighted. Water in the as-received oils was observable as very broad bands around 3300 cm^{-1}, 1625 cm^{-1}, and 550 cm^{-1}. At 120 °C, water was typically driven off in about 5 min. These are the persistant absorption bands of interest: saturated aliphatics (2950 – 2825 cm^{-1}, 1453 cm^{-1}, 1375 cm^{-1}, and 720 cm^{-1}); hydroxyl or amide hydrogen stretching vibrations (OH or NH, broad 3500–3100 cm^{-1}); a set of convoluted bands that includes carbonyls (mostly ketones or aldehydes, 1700 cm^{-1} or above; enols, quinones, or carboxylates may be 1650 cm^{-1} or below); phenyl ring stretching vibrations (broadly centered around 1600 cm^{-1}); and amides (amide I C═O stretch at 1650 cm^{-1}, and amide II NH deformation around 1550 cm^{-1}). Other identifiable peaks of interest at the low wavenumber range include those associated with out-of-plane bending of unsaturated CH groups, notably linear alkenes (*trans* at 966 cm^{-1} and *cis* at 700 cm^{-1}) and substituted phenyls (900–700 cm^{-1}) (Socrates, 2004).

In general, the spectra of all bio-oils show significant concentrations of polar groups such as carbonyls, hydroxyls, and amides; after thermal treatment, these polar groups can contribute to hardening of the bio-oil through strong intermolecular bonding. Depending on their exact nature, such groups can have a detrimental (as with carboxylates) or beneficial (as with amines or catechols) effect on the moisture susceptibility of asphalt binder. The bio-oils that don't harden as much after thermal treatment (Algae-2, WWS, and Algae-6) show significantly higher concentrations of saturated aliphatics. From the peak at 1600 cm^{-1}, Algae-3 seems to have the highest concentration of aromatic and polyaromatic compounds, which are common in petroleum bitumen (Hung and Fini, 2020; Hung and Fini, 2019).

After heat treatment, all bio-oils show increased intensity in the broad region around 1300–1100 cm^{-1} that is typically associated with a variety of C–O stretching bands, sulfates/sulfonates (SO_4/SO_3), and other groups. Most of the bio-oils also show some loss of aliphatics, although some of the decrease may be hidden by the choice of reference peak (1453 cm^{-1}). It is not immediately clear how much of the change is due to oxidation and how much is due to evaporative loss of small molecules. The evaporative loss of water is apparent in the spectra, but it may also hide other chemical changes such as condensation of hydroxyls or increased carbonyls. Another factor that complicates interpretation is that, without an independent standard to normalize the spectra, all percieved changes to absorption intensities can only be discussed relative to the choosen reference peak. Qualitatively, Algae-3 and Algae-6 appeared to be the least sensitive to thermal annealing.

Under the combined effects of heat and UV irradiation, bio-oils Algae-2, WWS, and Algae-6 showed significant increases in carbonyls and C–O groups. The other bio-oils were relatively insensitive to the addition of UV to heat exposure. Sensitivity to UV is not immediately indicative of poor performance; UV-sensitive materials may offer protection directly by adsorption of UV energy or indirectly by quenching radicals or forming a surface oxide layer that blocks further diffusion (Feng et al., 2013; Chin, 2007). It is notable that the three bio-oils with the highest concentration of aliphatics are also the most UV sensitive. Some of this sensitivity may arise from the presence of linear alkenes that are susceptible to peroxidation and free-radical generation through abstraction of hydrogen off α-carbons. However, alkenes cannot be the only contributing factor: Algae-5 was the bio-oil with the next highest concentration of alkenes, and it did not show UV sensitivity.

Fig. 3 shows the FTIR spectra of the room-temperature condensed vapors that emanated from the heated bio-oils. Compared to spectra of the bio-oils after thermal treatment, all of the vapors are enriched in aliphatics, most are enriched in ketones or aldehydes, and all are depleted in other polar groups. This evaporative loss of aliphatics is probably a significant cause of hardening of the bio-oils upon thermal annealing.

The enrichment of carbonyl compounds in the vapor is not unprecedented (Khare et al., 2020) and may partially explain the very small change in carbonyl content in the bio-oils themselves during thermal treatment. An increase in carbonyls (1710 cm^{-1}) is a common indicator of oxidative aging in petroleum bitumen. The fact that a similar increase is not observed in most of the bio-oils may be due to the relatively low temperature of the experiment (120 °C) in conjuction with some carbonyl compounds being lost to evaporation. Fig. 4 shows the change over time in the absorption intensity at selected wavenumbers (normalized to the total absorption of the fingerprint region) for bio-oils during the 1 h period of heating at 120 °C with or without UV. At 2924 cm^{-1} (CH_2 antisymmetric stretching vibration), most bio-oils show a moderate drop within the first 5 min before the rate of decline slows to a more constant rate. This trend could be indicative of the evaporative loss of aliphatics as well as increased oxidation (which increases the normalization factor). Algae-2 and WWS showed the steepest declines over time, and the decline is even steeper under UV exposure.

At 1601 cm^{-1} (phenyl ring stretch convoluted with various carbonyl bands and water), the trends are more complicated. Once again, significant changes within the first 5 min may be indicative of evaporative loss. Algae-1, Algae-3, and Algae-4 show trends of constantly decreasing intensity that may be the result of water loss or a relative increase in other polar groups such as C–O (Socrates, 2004). The intensity at this wavenumber stayed almost constant for Algae-5. With UV exposure, the rate of decline increased only slightly. In contrast, Algae-2, WWS, and Algae-6 showed increasing intensity at 1601 cm^{-1} with time at 120 °C and no UV, suggesting that carbonation may be occuring, increasing the relative concentration of aromatic and polyaromatic hydrocarbons. An alternate explanation is that the increase is the result of convolution with an increase in adjacent carbonyl bands, but the spectra shown in Fig. 2 appear to make this explanation unlikely. These samples also contained less water initially compared to the other bio-oils (except Algae-3), so any decline at this wavenumber due to water loss would be lessened. When UV irradiation is applied, the trend at 1601 cm^{-1} for Algae-2, WWS, and Algae-6 is an initial increase followed by a decline within the hour. Most likely, the decline is due to high oxidation rates increasing the normalization factor (total fingerprint intensity) as opposed to any significant decrease in aromatic concentration.

3.3. Thermal stability based on polarizability

The polarizability values serve as a measure of the electronic flexibility of the molecules within bio-oils, shedding light on their potential for intermolecular interactions and reactivity under varying conditions. Bio-oils with lower polarizability exhibited better resistance to both aging and moisture damage (Pahlavan et al., 2021; Rajib et al., 2020). However, it is essential to acknowledge that polarizability primarily informs us about the susceptibility of bio-oil components to oxidative agents and their ability to undergo electronic transitions. The observed

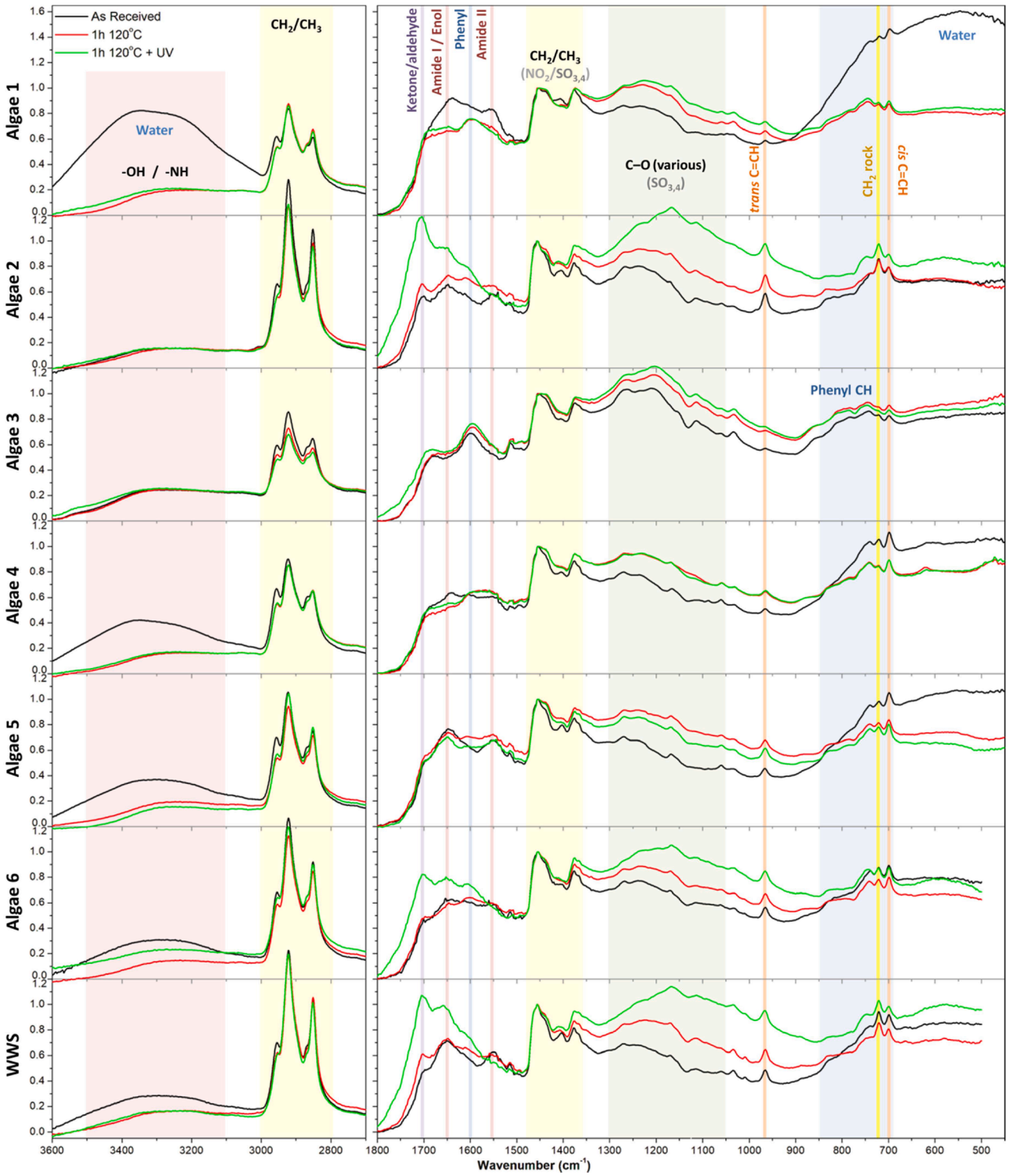

Fig. 2. FTIR of seven bio-oils as received (black), after 1 h at 120 °C (red), and after 1 h at 120 °C with 365 nm UV exposure (green). Select absorption bands are highlighted. Spectra were normalized to the peak at 1453 cm^{-1} for comparison.

responses of bio-oils to thermal stress encompass a broader spectrum of phenomena, including evaporation, condensation, and the generation of functional groups such as carbonyls. These multifaceted processes are not solely elucidated by polarizability data. Instead, polarizability offers a foundation for understanding the reactivity of bio-oil components, which, when coupled with the results of our experiments, collectively enriches our understanding of the observed thermal stability and response to UV exposure. Therefore, the integration of computational insights, such as polarizability, with observations from experiments offers a more comprehensive perspective on the suitability of bio-oils for diverse applications.

In our assessment of the polarizabilities of major compounds across seven provided bio-oils and WVO, the complexity of the resulting data makes direct comparisons difficult. Fig. 5 presents the polarizability results from our DFT calculations. In this figure, labels 1–5 are designated to represent the five predominant compounds present in each bio-

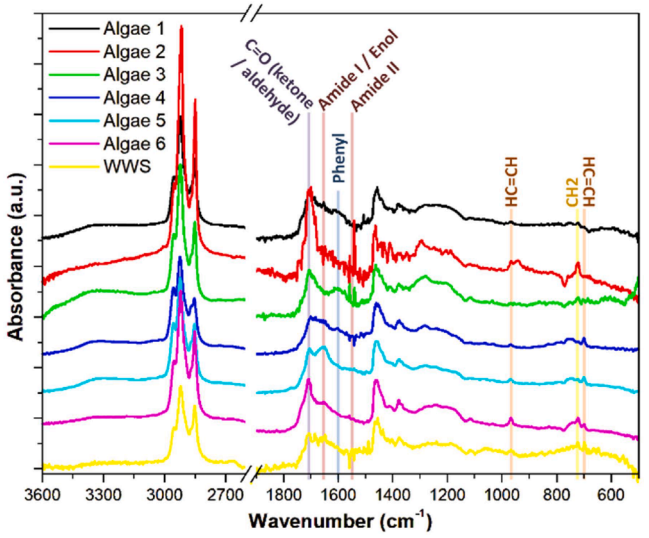

Fig. 3. FTIR spectra of vapors that emanated from the bio-oils during heating at 120 °C and that were condensed on a glass dish at room temperature.

oil sample, highlighting the key constituents that contribute to the sample's chemical profile and overall characteristics. The data provide a comprehensive insight into the potential reactivity and thermal vulnerability of the studied bio-oils. A case in point is Algae-3′s compound-1, which shows a substantially higher polarizability than its counterpart in other bio-oils. Such variability suggests that individual compounds within a bio-oil might demonstrate polarizability characteristics divergent from the collective behavior of the bio-oil's compounds. However, amidst these intricacies, a discernible trend emerges with Algae-1. It consistently presents the lowest polarizability across its five major compounds compared to the rest, setting itself apart from the cohort. This low polarizability indicates that the electron clouds of its molecules are less prone to distortion when subjected to external stimuli. In essence, their electrons remain more fixed and are not easily perturbed, pointing toward higher thermal stability. This inherent resilience, signaled by the consistent low polarizability of Algae-1′s compounds, suggests a robustness against thermal challenges, making it potentially one of the most thermally stable bio-oils in our study. As we shift from analyzing the polarizabilities of individual compounds to a broader view, the metrics of average polarizability and polarizability range become crucial. These measurements can provide clearer insights, especially when comparisons of individual compounds involve intricate patterns.

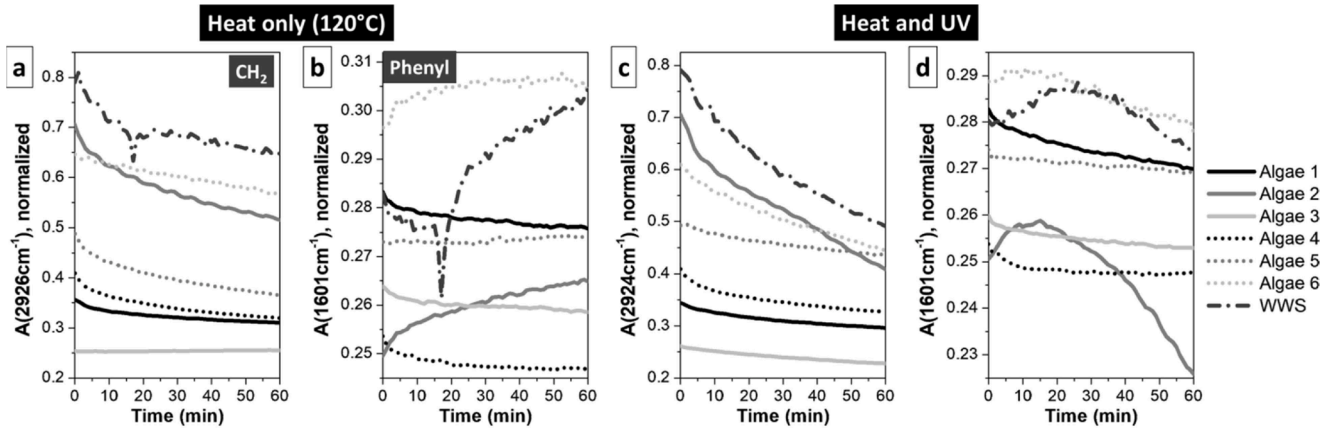

Fig. 4. Change in infrared absorption intensity at (a, c) 2924 cm^{-1} and (b, d) 1601 cm^{-1} over time for bio-oil samples exposed to (a, b) 120 °C heat or (c, d) both heat and UV. Absorption intensity was normalized to the integrated intensity of the fingerprint region (1860–450 cm^{-1}).

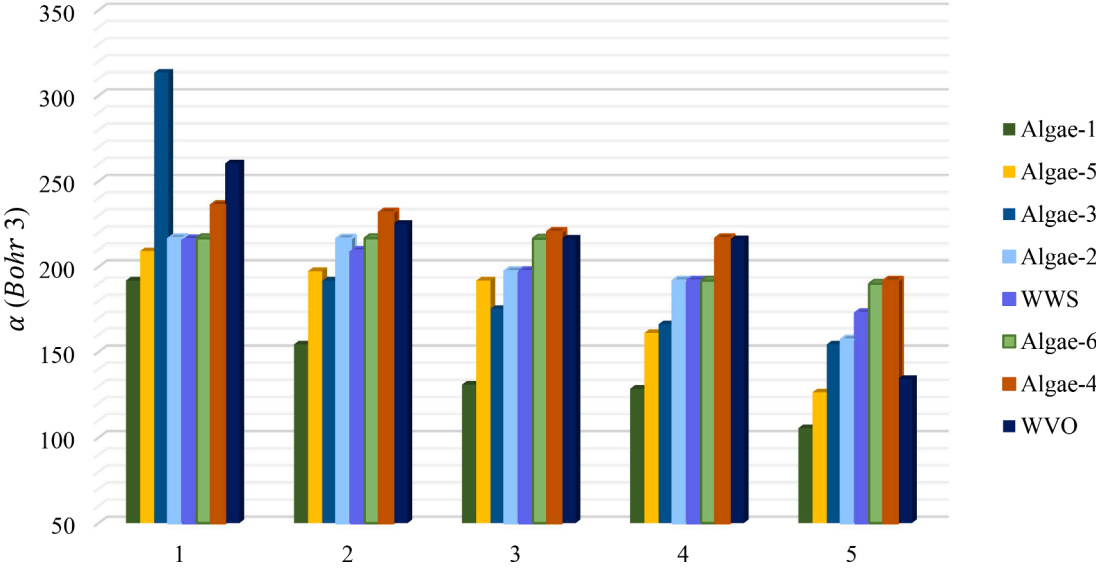

Fig. 5. Polarizability values of the five major compounds in seven bio-oils and WVO.

3.4. Average polarizability

Using average values in our analysis, as depicted in Fig. 6, offers a condensed metric that captures the overall behavior of a system, providing a clearer comparative perspective across various bio-oil samples. The average polarizability was obtained by summing the polarizability values of predominant compounds in each bio-oil and dividing by the total number of compounds, which in this case is five. In the context of polarizability, the average value serves as an indicative marker of a bio-oil compound's general susceptibility to external stimuli, particularly heat. A higher average polarizability typically suggests increased susceptibility to thermal changes, implying that the molecules within that bio-oil can more readily distort their electron clouds, enhancing their reactivity under thermal conditions. For instance, WVO, our benchmark, exhibited a specific polarizability value that sets a reference for our comparative analysis, illustrating distinct patterns in the average polarizabilities for the series of bio-oils.

Most bio-oils, with the notable exception of one standout, showed polarizability values that were lower than that of WVO, pointing toward greater thermal stability. The standout, Algae-4, manifested a polarizability markedly higher than WVO. This elevated polarizability suggests that relative to its counterparts, Algae-4 might be more susceptible to oxidative aging under thermal conditions.

Remarkably, Algae-1 boasts the lowest average polarizability within the group. This suggests a reduced vulnerability to external electric fields and hints at superior thermal stability compared to other bio-oils. While comprehensive understanding of this thermal resilience necessitates additional experiment studies, these preliminary findings provide valuable insight into the thermal behavior of these bio-oils.

3.5. Polarizability ranges

The polarizability range for each bio-oil was calculated by determining the difference between the highest and lowest polarizability values among the five predominant compounds in each sample. The polarizability range within each bio-oil is pivotal in offering insights into the inherent variability of its major compounds, as illustrated in Fig. 7. A bio-oil with a smaller polarizability range typically suggests that its major compounds have closely matched polarizabilities, leading to more consistent and predictable behaviors under thermal conditions. Conversely, a wider polarizability range indicates the presence of compounds with significantly different thermal stabilities, which could result in a variety of responses when exposed to similar thermal conditions.

When evaluating the thermal stability of bio-oils, consideration of both the average polarizability and the polarizability range provides a more comprehensive perspective. As examples, consider Algae-3, Algae-6, and WVO. Among the bio-oils studied, Algae-6 has one of the higher average polarizabilities at 206.35 Bohr (Qin et al., 2014), suggesting its compounds might be more reactive. Its narrow polarizability range of 26.63 units indicates that its major compounds are very similar in their thermal responses. This means that although the compounds in Algae-6 might be inherently more reactive (due to higher average polarizability), their reactions would be more uniform and consistent under thermal conditions, given the narrow range. In contrast, while Algae-3 has compounds that range from being highly stable to highly reactive (evidenced by its wide polarizability range of 159.11 units), its overall behavior can be less predictable under thermal conditions. This makes it crucial to weigh both the average and range when assessing an oil's overall thermal stability. The benchmark, WVO, has a polarizability range of 126.26 units, placing it higher than six of the seven bio-oils, which means it likely contains a broad mix of compounds in terms of their thermal stabilities.

3.6. Moisture-induced shear-thinning index (MISTI)

According to the literature, the shear-thinning value is sensitive to changes in the interface of bitumen and stone aggregates; the shear-thinning value is highly sensitive to changes in interfacial bonds (Oldham et al., 2022). The capability of the shear-thinning test to detect any changes at the interface has been shown by changing the surface chemistry of siliceous particles, altering the interfacial bond (Oldham et al., 2022). Here, the surface property of silica (as a surrogate for siliceous aggregates) is altered by bio-oil. Fig. 8 shows the shear-thinning values for the control and bio-modified binders (at dosages of 3 % and 6 %). The interaction between the bitumen and the glass beads is closely related to the shear-thinning value; a steeper shear-thinning value indicates greater interaction between the bitumen and the glass beads (Aldagari et al., 2022; Faisal Kabir et al., 2021; Rajib et al., 2021). It can be seen that all bio-oils enhanced the intermolecular interaction at the interface when the inclusion of bio-oil was at 3 %, as shown by higher shear-thinning values compared to the control binder. This indicates the effectiveness of the bio-oil in promoting intermolecular interactions between the bitumen and aggregates. Conversely, a

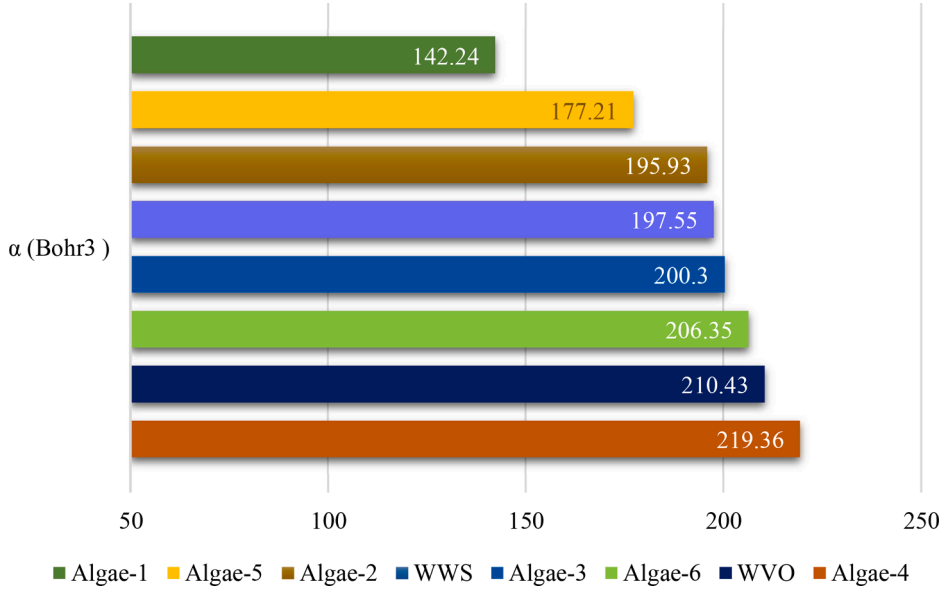

Fig. 6. Average polarizability values of the major compounds in seven bio-oils and WVO.

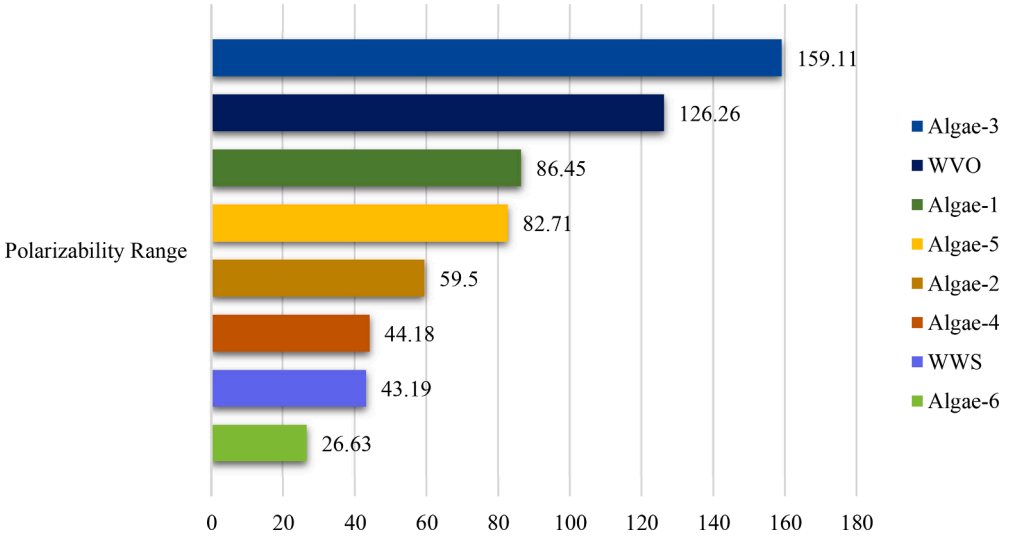

Fig. 7. Polarizability range values of the major compounds in seven bio-oils and WVO.

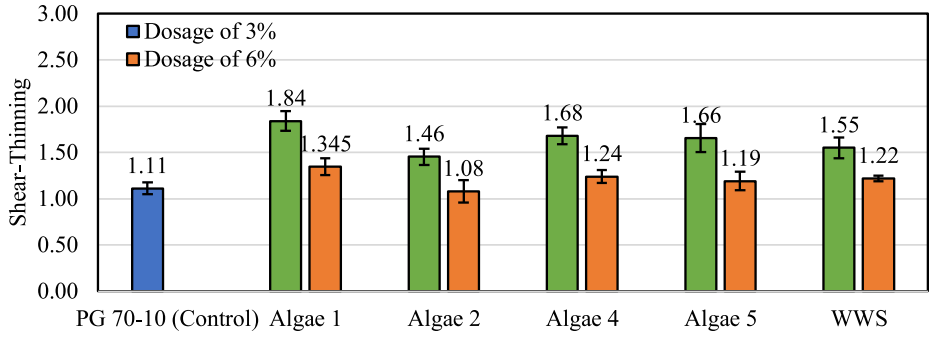

Fig. 8. Shear-thinning values for control bitumen and bitumen modified with each of five bio-oils.

greater dosage of bio-oil (6 %) had a negative impact on the interaction, as evidenced by a reduction in the shear-thinning values compared to the ones obtained from a dosage of 3 %.

The observed trends in intermolecular interactions between bio-oil-modified binders and aggregates can be attributed to the dosage-dependent nature of the bio-oil's influence. At a 3 % dosage, the bio-oil effectively enhanced intermolecular interactions, leading to higher shear-thinning values compared to the control binder. This improvement is likely due to the presence of functional groups in the bio-oil that facilitate bonding with the bitumen and aggregates. However, at a higher dosage of 6 %, a contrasting effect is observed. The excessive concentration of bio-oil may lead to overcrowding at the interface, hindering effective interactions between the binder and aggregates. This overcrowding effect can impede the ability of the bio-oil to promote intermolecular bonding, resulting in a reduction in shear-thinning values compared to the 3 % dosage. Therefore, the dosage-dependent impact on intermolecular interactions can be attributed to the balance between the bio-oil's beneficial effects at lower dosages and potential overcrowding at higher dosages. From the findings presented in Fig. 8, the remarkable strength of interaction observed with Algae-1 at a 3 % bio-oil dosage can be attributed to the specific molecular components present in this bio-oil and their intricate interactions with the bitumen and aggregates. Algae-1 contains several key constituents that contribute to its superior performance. First, n-Hexadecanoic acid, a long-chain fatty acid in the bio-oil, is known for its capacity to form hydrogen bonds with polar functional groups, which are potentially present in bitumen and aggregates. The carboxylic acid (-COOH) moiety in n-Hexadecanoic acid facilitates hydrogen bonding, fostering strong intermolecular interactions. Additionally, the presence of aliphatic hydrocarbons such as Tetradecane, Dodecane, and Tridecane in Algae-1 provides further support for enhanced interaction. Despite their nonpolar nature, the extended alkane chains in these compounds can create physical entanglements with bitumen molecules, promoting improved adhesion and shear-thinning behavior. Moreover, the inclusion of Sulfurous Acid, 2-Ethylhexyl Heptadecyl Ester, with its sulfur-containing functional groups, opens the door to potential interactions with polar functional groups in bitumen or aggregates. These various molecular interactions culminate in a favorable intermolecular environment at the bitumen-aggregate interface, resulting in enhanced shear-thinning behavior and robust intermolecular bonding, as evidenced in the results of the experiments.

Fig. 9 shows the deviation of the MISTI value from the value of 1 for bitumens containing bio-oil. A lower MISTI deviation from 1 indicates better resistance to moisture damage (Aldagari et al., 2022; Faisal Kabir et al., 2021; Oldham et al., 2022). The susceptibility of all bio-modified binders to moisture damage was higher compared to the control binder, as shown by higher MISTI deviations from one. In addition, a greater dosage of bio-oil (6 %) increased the moisture susceptibility, as evidenced by an increase in MISTI deviation compared to the values obtained from a dosage of 3 %. These observations regarding moisture susceptibility can be attributed to some reactive groups present in bio-oils that can adhere well with siliceous surfaces in dry conditions; however, these groups can easily be displaced later by water, so the bio-modified binder has moisture susceptibility. Further insights from our previous research on acid accumulation indicate that the presence of carboxylic acid compounds in bio-oils increases the susceptibility to

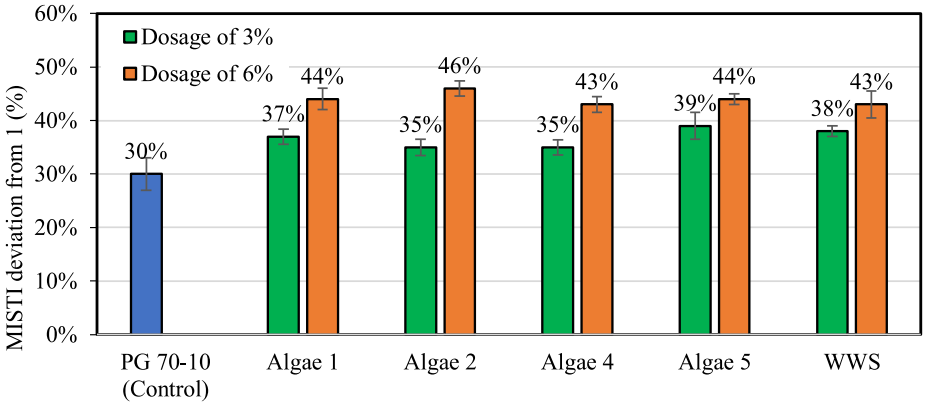

Fig. 9. MISTI deviation from 1 for control bitumen and bitumens modified with bio-oil.

moisture damage in asphalt binders modified with these bio-oils (Hung et al., 2019). As these acids accumulate and crystallize at the bitumen-siliceous stone aggregate interface, they can trigger hydrolysis, increasing possibility of moisture damage in pavements.

Fig. 9 shows the MISTI values for five of the bio-oils tested at a 6 % dosage. Algae-2 exhibited the highest moisture susceptibility, as evidenced by our laboratory testing. This increased vulnerability to moisture in Algae-2 bio-oil can be attributed to the dominant component of Algae-2, which was identified as having a substantial presence of acids, particularly carboxylic acids. These acidic compounds accounted for a significant portion of the total GC–MS area in Algae-2 bio-oil. The affinity of carboxylic acids to siliceous surfaces in dry conditions and their ease of displacement by water is shown in prior works (Hung et al., 2019). The high concentration of carboxylic acids in Algae-2 bio-oil likely contributes to the observed increase in the moisture susceptibility, rendering pavements more susceptible to moisture damage. This result underscores the significance of understanding the chemical composition of bio-oils, specifically the presence of acidic compounds, when assessing their suitability for BioPave applications. The findings emphasize the need for careful consideration of bio-oil properties to ensure their effectiveness and durability in a paving mixtures.

4. Conclusions

The use of bio-oils as sustainable alternatives in construction materials has garnered significant attention in recent years because of their potential to reduce environmental impact. This study aimed to comprehensively investigate various aspects of bio-oils derived from diverse biowaste sources, with a focus on their behavior under different conditions and their suitability for construction applications. These are the findings of this study:

- All bio-oils solidified upon cooling after a mild heating, primarily because of the evaporation of aliphatic compounds of low molecular weight. Some of the solidified bio-oils exhibited hardness and brittleness, attributed to their high concentrations of polar groups such as carbonyls, hydroxyls, and amides. Notably, Algae-2, WWS, and Algae-6, initially high in aliphatic content, remained relatively ductile upon heating.
- Algae-2, WWS, and Algae-6, initially high in aliphatic content, also exhibited the high reactivity to UV exposure. While this doesn't necessarily indicate susceptibility to solar degradation and may even suggest protective effects in some cases, their exceptional UV sensitivity warrants further evaluation.
- Algae-1, Algae-4, and Algae-5 initially contained the most water. Even though this water is quickly evaporated at elevated temperatures, the oils' ability to absorb more water raises concerns about their resistance to moisture damage.
- Shear-thinning test results underscore the dosage-dependent influence of bio-oil on intermolecular interactions at the bitumen-aggregate interface. At a 3 % dosage, bio-oil enhances these interactions, leading to higher shear-thinning values compared to the control binder. However, at a higher dosage of 6 %, the bio-oil's excessive concentration can hinder effective intermolecular bonding, resulting in a reduction in shear-thinning values. These findings emphasize the critical role of bio-oil dosage in optimizing the bitumen-aggregate interface for improved BioPave performance. Algae-1 at a 3 % bio-oil dosage showed a remarkable capacity to enhance shear-thinning behavior and robust intermolecular bonding, underscoring its potential for improving bitumen-aggregate interactions.
- The MISTI test showed that binders modified with bio-oil had increased susceptibility to moisture compared to the control binder, with a 6 % dosage of bio-oil exacerbating this effect. This increased susceptibility to moisture is attributed to bio-oil's reactive surface-adhering groups, which are vulnerable to water-induced removal. Algae-2 bio-oil, characterized by a dominant component of carboxylic acids, showed the highest susceptibility to moisture. The presence of these acids, prominent in the GC–MS analysis, intensifies moisture-induced pavement distress.
- Most of the bio-oils, especially Algae-1, consistently demonstrated lower polarizability across their major compounds, suggesting higher thermal stability compared to the others. Specifically, Algae-1 stood out as potentially the most thermally stable bio-oil in the study.
- Using average polarizability values as a benchmark, the majority of bio-oils showed greater thermal stabilities than WVO, with Algae-1 having the lowest average polarizability. However, Algae-4 exhibited a polarizability significantly higher than WVO, indicating a potential vulnerability to oxidative aging under thermal conditions.
- The polarizability range offers insights into the inherent variability of the compounds within each bio-oil. A narrower range suggests more consistent thermal responses across major compounds, while a wider range indicates a potential mix of highly stable to highly reactive compounds. For instance, Algae-6, despite having a higher average polarizability, exhibits a consistent thermal response because of its narrow polarizability range.

Our study's findings have significant implications for the development of sustainable construction materials, particularly in the innovative application of bio-oils in pavement technologies like 'BioPave'. The research contributes to a deeper understanding of how different bio-oils, derived from various biowaste sources, behave under environmental stressors such as thermal and solar radiation, and moisture, thereby informing their practical applications in outdoor construction.

Looking forward, the study opens several avenues for future research. These include exploring the long-term performance of bio-oil

modified construction materials in real-world environmental conditions, assessing the economic and environmental feasibility of scaling up bio-oil usage in construction, and refining bio-oil processing methods to optimize their performance in construction applications. These ongoing research efforts are essential for advancing the field of sustainable construction materials and addressing the current challenges in utilizing bio-oils for improved pavement performance and environmental sustainability.

CRediT authorship contribution statement

Farideh Pahlavan: Writing – original draft, Visualization, Methodology, Formal analysis. **Albert M. Hung:** Writing – original draft, Visualization, Methodology, Formal analysis. **Sand Aldagari:** Writing – original draft, Visualization, Methodology, Formal analysis. **Andrew J. Schmidt:** Writing – review & editing, Data curation, Validation. **Peter J. Valdez:** Funding acquisition, Writing – review & editing, Data curation, Validation. **Elham H. Fini:** Conceptualization, Funding acquisition, Supervision, Validation, Writing – review & editing.

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.

Data availability

All data used has been reported in the paper.

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Supplementary materials

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