USING FTIR ANALYSIS TO EXAMINE AGING SUSCEPTIBILITY ON BIO-ASPHALTS MODIFIED BY BLACK SOLDIER FLY LARVAE OIL

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by
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Abstract

USING FTIR ANALYSIS TO EXAMINE AGING SUSCEPTIBILITY ON BIO-ASPHALTS MODIFIED BY BLACK SOLDIER FLY LARVAE OIL

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This thesis provides foundational research on bio-asphalts and specifically investigates the modification of petroleum-based asphalt binder with bio-based black soldier fly larvae oil (BSFLO) using Fourier-transform infrared spectroscopy (FTIR) analysis. This study aims to assess the effect of BSFLO on the aging resistance of conventional asphalt binder. The BSFLO used in this study is EnviroOil, which is produced from mechanically pressing dried larvae and trademarked by EnviroFlight. The four research questions answered in this paper are related to using FTIR analysis for identifying modifiers in asphalt binder and calculating carbonyl (C=O) index. No significant differences were found between aged PG 70-22 and PG 64-22 asphalt binders and aged bio-asphalts so, additions of 5, 10, and 20% BSFLO by weight to asphalt binder could potentially be applied with no effect on aging resistance. The compatibility of the IR spectra of asphalt binder, BSFLO, and bio-asphalts is also discussed. This thesis includes a review of relevant literature, provides information on bio-asphalt production, and describes methods and analysis in using FTIR to evaluate aging susceptibility in asphalt binder modified with the addition of 5, 10, and 20% BSFLO by weight.

Keywords: Bio-Asphalt, Asphalt Binder, Bio-Oil, Black Soldier Fly Larvae Oil, Aging Susceptibility, Fourier-Transform Infrared Spectroscopy
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Introduction

Solutions to our sustainability crises lie in resource management, closed-loop systems, and renewable materials. As renewable resources become more researched, sustainable solutions are being found in waste products that can aid in the decreased use or full and partial replacement of fossil fuels. This work aims to study the aging resistance of bio-based oil modified asphalt binder using Fourier-transform infrared spectroscopy (FTIR). The origins of raw materials used in the asphalt industry are a crucial part of why bio-based oil is being studied so, the difference in biomass collection versus fossil fuel extraction is significant. First the importance of biomass waste collection and transformation will be outlined, including agricultural waste streams and the role of black soldier fly larvae (BSFL) in composting and biomass transformation. Then the production of bio-based oils including bio-oil (BO), BSFL oil (BSFLO), and waste cooking oil (WCO) will be introduced. Next the role of these oils in bio-based asphalt binder, or bio-asphalt, will be discussed along with the use of FTIR testing technology in the bio-asphalt industry.

BSFL Composting

Biomass waste is an example of squandered resources and has benefits of being widely accessible, available, and renewable, and therefore should be reused (Erdogdu et al., 2018). For example, agricultural industries can create significant amounts of wasted biomass causing waste disposal issues and environmental impacts, especially in livestock production (Pandey et al., 2019). Biomass is recognized as a valuable raw material for creating soil amendments but also for chemical conversion and fuel production (Erdogdu et al., 2018). Biomass comes from plant-based and animal-based sources in forms of vegetable wastes, animal byproducts, and other organic matter (OM), and all should be treated as valuable resources (Wang et al., 2020).
When buried in landfills, OM anaerobically digests which produces methane, the most potent greenhouse gas (Shelomi, 2020). OM increases the weight of transported trash and takes up unnecessary space in landfills (Shelomi, 2020). Diverting OM from the landfill and composting instead is one option for appropriately dealing with OM. Composting traditionally is the bioconversion of OM into a usable and valuable soil amendment used in agricultural productions (Makan & Fadili, 2020). Due to downsides of traditional composting, compost production is disincentivized on a small- and large-scale (Zouzias, 2021). However, the cultivation of BSFL on OM incentivizes the diversion of food waste and OM from landfills for many reasons. One being that BSFL composting (BSFLC) produces two valuable materials. The bioconversion of OM to BSFL is not only used to manage OM more efficiently than traditional composting, but the larvae themselves become valuable protein packed livestock feed with a high fat concentration allowing them to also be great candidates for bio-based oil production (Zouzias, 2021). Processes such as composting, and bio-based oil production, incentivize reutilizing these OM waste streams.

**BO Production Process**

Usually, thermochemical conversion or thermal degradation, such as fast pyrolysis, of varying types of biomasses are used to produce BO, a renewable substitute for petroleum oil (Wang et al., 2020). BO, or pyrolysis oil, has the potential to replace petroleum-based products partially or fully in a multitude of industries due to chemical structure compatibility (Wang et al., 2020). Each biomass creates a complicated chemical composition that can be altered to produce varying types of BO (Wang et al., 2020). More popular biomasses used in pyrolysis for BO production range from animal manure to switchgrass or tree bark (Wang et al., 2020).
**BSFLO Production Process**

Multiple types of oils have been used in asphalt binder production and rejuvenation (Zahoor et al., 2021). WCOs have been utilized as an alternative to BO. They are collected from cooking processes and are originally produced through mechanical pressing rather than fast pyrolysis (Khedaywi & Melhem, 2022). BSFLO is produced from dried BSFL, and the oil is also mechanically pressed from the dried larvae, providing high fat oil, similar to coconut and palm kernel oils (EnviroFlight, 2022). BSFLO is being scrutinized due to the scalable production of BSFL on waste-streams and in turn its ability to provide multiple products with widely available inputs that would normally be landfilled (Lalander et al., 2020). BSFLC incentivizes the utilization of wasted OM while providing biomass for use in bio-based oil production.

**Bio-Asphalt Production Process**

Specifically in the asphalt industry, bio-based oils are being researched for their ability to replace petroleum-based asphalt binder in asphalt pavement construction to decrease the carbon emissions of this industry (Wang et al., 2020). The use of bio-based oils in asphalt binder for asphalt production is promising. The two main advantages are the use of waste which decreases the number of materials being landfilled and the reduction in the use of virgin asphalt binder which reduces greenhouse gas emissions and carbon footprint of the asphalt pavement construction industry (Wang et al., 2020). The partial replacement of asphalt binder in road engineering with bio-based oils may result in a significant decrease in the cost of binders in construction and possible decrease in maintenance costs (Wang et al., 2020). Animal and vegetable WCOs have also been used in asphalt binder rejuvenation to reinstate basic properties in aged asphalt binder (Zahoor et al., 2021). One disadvantage of bio-based oils is high oxygen content that can increase oxidative aging and moreover, oxidative aging is a known culprit in
chemically changing asphalt binder to become prone to cracking (Cao et al., 2019; Wang et al., 2020; Zhang et al., 2020). This makes the effects of aging resistance an important topic for bio-based oil modification of asphalt binder. A comparison of BSFLO to petroleum-based asphalt binders will aid in determining the potential of BSFLO modified asphalt binder or BSFL bio-asphalt performance. The bio-based oil samples that have the most compatibility in chemical structure and shared properties to petroleum-based asphalt binder will be most important for further testing as a modifier in asphalt binder (Wang et al., 2020). Bio-based oils have shown to have promising benefits in terms of asphalt rejuvenation and preventing failures due to aging (Ghosh et al., 2018).

**FTIR**

FTIR is a method used to obtain an infrared spectrum that shows how molecules in a material structure absorb energy or radiation of a defined wavenumber (Lim et al., 2022). FTIR is used to identify compounds and analyze structures to determine functional groups through varying wavelengths of radiation being absorbed (Zhang, Han, et al., 2021). IR spectra can be used to examine the chemical structure of bio-based oils and evaluate their compatibility with petroleum-based asphalt binder (Wang et al., 2020). By studying the IR spectra, the chemical composition of BO and cooking oils are similar to that of asphalt showing feasibility for replacement of petroleum-based binder with bio-based oil (Wan Azahar et al., 2016; Wang et al., 2020). FTIR is a popular method to examine chemical compositional changes due to oxidative aging (Hofko et al., 2018).
Problem Statement

Asphalt is the main raw material in civil engineering and its use and maintenance is crucial in road engineering (Wang et al., 2020). According to the National Pavement Association, more than 94% of the 2.7 million miles of paved road in the US are surfaced with asphalt binder (Karnati et al., 2019). For the industry questions about the increasing price and decreasing supply of crude oil are imminent (Cao et al., 2019). Not only is the collection and use of crude oil putting disastrous pressure on the living environment, but it is also a nonrenewable resource that we depend heavily on. Replacing crude oil even partially in asphalt with alternative sustainable resources will have a dramatic effect on the industry (Cao et al., 2019). Using BO to replace crude oil in road engineering, will greatly reduce the monetary and environmental cost of binders in construction (Wang et al., 2020). Aging resistance is a major factor in the deformation of pavement (Lim et al., 2022). As bio-based oils are being studied for use in asphalt pavement applications, a major issue with this approach is high aging susceptibility of bio-based oil modified asphalt binder. So, providing incentive to use bio-based oil modified asphalt binder by showing aging resistance is important and needs to be investigated.

Research Questions

1. How does the IR spectra of BSFLO modified asphalt binder or BSFL bio-asphalts compare to petroleum-based asphalt binder through a FTIR test?
2. How does the carbonyl index of the IR spectra demonstrate the aging susceptibility of asphalt binder?
3. How does FTIR demonstrate the effect of BSFLO on aging resistance of asphalt binder?
4. Does BSFLO increase or decrease aging resistance in asphalt binders according to IR spectra?
Limitations

For this study there was no access to or use of rolling thin-film oven test (RTFOT) or pressure aging vessel (PAV) equipment, so it does not follow ASTM standards for the asphalt industry. Variabilities could be found in bio-asphalt samples created for this study. The only known manufacturing details for the BSFLO used in this study are that it uses dried BSFL in a mechanical press and so, specific temperatures, pressures and methods are not included. A better understanding of the BSFLO being used along with more samples and further testing recommended before applying BSFLO modified asphalt binder.

Overview of Document

Within this document is a review of literature, an overview of research methodology, data from the study, and analysis and discussion of the results.

Literature Review

The purpose of the literature review is to explain and define the use of BSFL in biomass transformation along with the production and evaluation of bio-based oils. The term bio-based oil encompasses all types of oil produced from biomass, or any living matter in which solar energy is stored, while BO refers to pyrolysis oil (Zhang et al., 2020; Zhang, You, et al., 2021). Asphalt and bio-asphalt production and performance will be explained. Different properties such as anti-aging are included along with the use of FTIR to distinguish the effects of service life on asphalt binder.
BSFL Composting

With worldwide challenges of managing resources from waste streams to raw materials there is pressure to be sustainable with an ever-increasing population and decreasing amount of fossil fuel sources. Not only does OM decompose anaerobically in landfills producing methane, a greenhouse gas, it is a useful resource for biomass transformation. Composting organic waste is one way of biomass transformation and resource management that is an advancing branch of waste removal, storage, and recycling (Gershuny & Martin, 2018). Determining alternative ways to handle manure, food waste, and other organic matter is important as the expanding rate of waste production affects public health and environmental stability (Liu et al., 2019). Traditional composting converts OM into a soil-like substance that is uniform in structure, which can be used as organic fertilizer or to remediate infertile and depleted land (Weppen, 2001).

A more appropriate method regarding organic waste management is using BSFL which naturally convert manure and OM into fertilizer and larvae biomass. A saprophytic insect, the black soldier fly can be found in tropical, subtropical, and warm temperate regions around the world (Guo et al., 2021). The four stages of growth for the black soldier fly include egg, larva, pupa, and adult (Guo et al., 2021). The larvae, which consume about 200 mg per day, feed on OM, usually decaying organisms, food waste, and manure (Attiogbe et al., 2019). Their ability to consume 15 times their own weight in one week and be safe insects to work with, makes them ideal for composting, zero waste applications and farmers (Shelomi, 2020). Dried larva biomass is 40% protein and high in fat content, which is primarily used as a protein source in animal feed (Lalander et al., 2020). Other uses for BSFL include fish meal alternatives, oil production, biodiesel production, and anaerobic digestion feedstock (EnviroFlight, 2022; Lalander et al.,
BSFLC effectively manages waste and produces larvae high in protein and fat while maintaining a low cost of operation and sustainable waste recycling system (Liu et al., 2019).

The downsides to composting that disincentivize municipal composting systems include transportation costs, long timelines, ample space, and low payback ability (Shelomi, 2020). However, with BSFL the bulk density of food waste inputs is decreased quickly, the processing timeline is greatly reduced, less space is required, and profitable larvae are produced (Zouzias, 2021). By preserving and containing a small percentage of larvae produced in the system to pupate into flies, black soldier flies in the BSFLC system will continuously lay eggs on fresh OM and therefore self-habituate the system (Zouzias, 2021). The biotreatment of food waste using BSFL could reduce CH₄, N₂O, and NH₃ emissions when compared to traditional composting methods (Pang et al., 2019). BSFLC becomes a self-habituating, closed-loop system for handling wasted OM with BSFL and produces larvae biomass that can be used as livestock feed or used in oil production (EnviroFlight, 2022; Shelomi, 2020). BSFLC incentivizes biomass collection and reuse providing opportunities for biomass transformation to deliver products that can then be used in asphalt binder substitutions.

**BO Production**

The varying types of thermochemical conversion methods and biomasses used in BO production affect the outcome of products. Solids, liquids, and gases can be produced by the thermal degradation of biomass in anaerobic conditions (Goyal et al., 2008). Thermochemical conversion approaches include gasification, liquefaction, and pyrolysis. The fast pyrolysis method has the highest BO yield (Zhang et al., 2020). Fast pyrolysis is completed at high temperatures in the absence of oxygen (Ali et al., 2015). Pyrolysis provides flexibility in its ability to convert biomass into various products. There are three temperature ranges for
pyrolysis: fast pyrolysis is done at temperatures equal or greater than 500°C, slow pyrolysis decreases the rate it reaches high temperatures, and low temperature carbonization is equal or lower than 400°C (Akhtar & Saidina Amin, 2012). Slow pyrolysis is usually used to produce solid materials such as biochar. Fast pyrolysis is usually used to produce liquids like BO (Zhang et al., 2020).

In the production of BO, or pyrolysis oil, the fast pyrolysis method is most researched and accepted for the highest output of BO with the least resource inputs (Goyal et al., 2008). The properties and quantity of BO are determined by the biomass feedstock and pyrolysis conditions (Li et al., 2021). Pyrolysis conditions include the temperature, particle size, heating rate, and total time of the process (Li et al., 2021).

**Biomass Type**

Biomass is a resource available worldwide that has been recognized as a valuable raw material for chemical and fuel production (Erdogdu et al., 2018). Biomass consists of organic and inorganic compounds which affect pyrolysis outputs and the extent of decomposition (Akhtar & Saidina Amin, 2012). Biomass type plays a significant role in pyrolysis and bio-based oil production. There are two branches of biomass that are woody, which means coming from plants, and non-woody, coming from excess waste of animals and industry (Kabir Ahmad et al., 2020). Plant-based and animal-based sources of biomass that BO can be extracted from are all prepared and processed differently (Wang et al., 2020).

Biomass is composed of lignin, cellulose, hemicelluloses, and minute amounts of inorganic matter (Akhtar & Saidina Amin, 2012). One study explained that usually a lignin-rich liquid fuel, BO yield is maximized in fast pyrolysis (Wang et al., 2020). Agricultural wastes, including animal-based, or non-woody biomasses, compared to plant based or woody biomasses are both
usually characterized by organic and inorganic compounds, with few studies using cellulose, hemicellulose, or lignin analyses for animal-based biomass. Providing a consistent feedstock for thermochemical conversion depends on biomass growth and access. Blending provides a specific chemical composition through intentionally mixing biomass feedstocks and can aid in this consistency (Edmunds et al., 2018).

**Bio-Oil**

BO, or biocrude oil, is a complicated fuel due to the excessive number of various components that affect its capability as a reliable fuel. About 200 different organic compounds can be found in it (Erdogdu et al., 2018). Biocrude oils derived from poultry litter and other biomasses are more viscous and unstable compared to petroleum fuels (Pandey et al., 2019). BOs can have ranging pH and calorific values (Pandey et al., 2019). Poultry litter is high in protein and nitrogen which creates a higher calorific value than hardwood biocrude oil (Pandey et al., 2019). Disadvantages of raw BO include high water content, high oxygen content, low heating value, low pH, complicated composition, and instability (Wang et al., 2020). Even though replacing petroleum-based oils with bio-based oils is ideal for environmental benefits, the high oxygen content in bio-based oils is linked to high oxidative aging and moreover, oxidative aging has proven to cause deformations in asphalt binder composition, making the investigation of aging resistance an important area of research for BO and other bio-based oil modified asphalt binders (Cao et al., 2019; Zhang et al., 2020).

**BSFLO**

Alternative to fast pyrolysis and BO production is the reuse of cooking oils and production of oils through mechanical pressing. These oils contain light oil components comparable to those of the virgin bitumen (Zahoor et al., 2021). BSFLO is mechanically pressed
from dried BSFL, providing high fat oil, similar to other vegetable oils (EnviroFlight, 2022). WCOs, or waste animal and plant based edible oils, are mostly used in the process of rejuvenation where hard and brittle asphalt binder is mixed with virgin bitumen and oil to restore the structural and functional properties of the binder (Zahoor et al., 2021). However, it can be used directly in virgin asphalt binder (Zahoor et al., 2021). WCOs have been used to produce pyrolysis oil as well (Cao, et al., 2019). Due to changes in the chemical composition of asphalt over time which decreases its effectiveness and performance, maintenance and rehabilitation is required (Zhang, Han, et al., 2021). One study showed promising results in the ability of residual soybean oil being used as a rejuvenator for aged asphalt binder (Zhang, Han, et al., 2021). Soybean oil waste can be reused in recycling applications that could provide sustainable and cost-effective alternatives for asphalt pavement regeneration technologies (Zhang, Han, et al., 2021). There are advantages of low volatility and low toxicity in the use of bio-based oils in asphalt binder rejuvenators (Zhang, Han, et al., 2021). Rejuvenators can reverse the aging process to make aged asphalt binder recyclable (Zhang, Han, et al., 2021).

The chemical properties of WCO have an impact on its blending with asphalt binder (Zahoor et al., 2021). Characterizing the chemical and functional groups of WCO modifiers for asphalt binder conducted with FTIR can relay compatibility (Wan Azahar et al., 2016). It is emphasized by studies to identify chemical structure and composition of modifiers to asphalt binder with FTIR before researching effects of modifiers on performance (Wan Azahar et al., 2016). Through FTIR observation there are the same types of functional groups existing in WCO and asphalt binder through the C-H bond (alkyl) (Wan Azahar et al., 2016). BSFLO and cooking oil fall into the category of mechanically pressed oils and their functional groups in IR spectra are similar to each other and to asphalt binder creating a potential new use of BSFLO in asphalt
binder modification that should be explored (Wan Azahar et al., 2016; Zahoor et al., 2021; Zozo et al., 2022).

**Bio-Asphalt**

**Bio-Asphalt Preparation**

Asphalt is a construction material that is a mixture of asphalt binder, course and fine aggregate, and additional agents (Zhang, You, et al., 2021). Its use in paving roads requires a material resistant to high and low temperatures, aging, moisture, and other environmental effects. Bio-based oil modified asphalt, or bio-asphalt, is created by blending bio-based oils and asphalt binders with different mixing temperatures, mixing times, and shear rates (Zhang, You, et al., 2021). These bio-asphalts can struggle to perform at high temperatures and can exhibit faster aging (Zhang, You, et al., 2021). The use of BO or other bio-based oils in asphalt binder changes the asphalt chemical composition and therefore its resilience and degradation. This chemical composition will also be altered under environmental impacts such as high temperatures, oxygen, moisture, and UV radiation (Zhang, You, et al., 2021). Chemical changes occur under oxidative aging through the shifting of light, non-polar fractions to heavy, polar components (Cao et al., 2019). This makes asphalt binder material stiffer and therefore more prone to cracking (Cao et al., 2019). Bio-asphalt has been tested for differences in properties and performance compared to petroleum-based asphalt binder. Even though it depends on the biomass source, overall performances of BO modified asphalt binders showed a negative impact on high-temperature performance and a positive impact on low-temperature performance (Zhang, You, et al., 2021). Even with a slight decrease in high-temperature stability of aged asphalt, BO can improve aging resistance, penetration, and ductility and reduce its softening point and viscosity which shows beneficial rejuvenation effects on the performance of aged asphalt (Zhang et al., 2020). There
was great variability in intermediate temperature performance and moisture susceptibility (Zhang, You, et al., 2021). However, another source found that the workability and high-temperature performance of most asphalt was enhanced after adding BO, while low-temperature performance reduced (Wang et al., 2020). The preparation of bio-asphalt compared to conventional asphalt showed a lower environmental impact (Zhang et al., 2020). Overall, the use of BO and other bio-based oils is promising and could significantly reduce costs of binders in road construction while decreasing greenhouse gas emissions (Wang et al., 2020).

The effectiveness of bio-asphalt is mostly dependent on the biomass source. Animal and plant-based bio-asphalts create variabilities in low and high temperatures reactions and its workability (Zhang, You, et al., 2021). By using petroleum-based asphalt binder as the control there are many studies on its comparison to bio-asphalts with different types of biomasses used. The variability in BO characteristics due to types and preparations of biomass used can create unwanted properties in bio-asphalt (Zhang, You, et al., 2021). There is more resistance to aging in swine manure-based bio-asphalts than plant-based bio-asphalts (Zhang, You, et al., 2021). Waste wood and swine manure BOs have also shown an increase in low-temperature fracture resistance and workability; however, a reduction was seen in its high-temperature qualities (Zhang, You, et al., 2021). Sawdust BO had promising compatibility with petroleum asphalt (Zhang, You, et al., 2021). Also, blending biomass types and BOs has created opportunities for improving performance and dependability in asphalt binder use (Zhang, You, et al., 2021). The high amount of oxygen element and less carbon element in switchgrass BO and other plant-based BOs than in petroleum-based asphalt binder can make BOs prone to aging (Zhang, You, et al., 2021).
Studies have been conducted on asphalt binder using different types of oil additives including petroleum-derived oils, bio-based oils, refined waste motor oil, and WCOs (Lei et al., 2017; Zahoor et al., 2021). Animal and vegetable WCOs have been seen to reinstate basic properties in aged asphalt binder (Zahoor et al., 2021). WCOs and BSFLO are extracted through mechanical pressing (EnviroFlight, 2022; Khedaywi & Melhem, 2022). Researchers have agreed that waste vegetable oil can aid in thermal cracking resistance and reduced viscosity in asphalt binder (Khedaywi & Melhem, 2022). BSFLO has a similar chemical structure to cooking oils and therefore could have potential in bio-asphalt production and aged asphalt rejuvenation (Zahoor et al., 2021; Zozo et al., 2022).

**Chemical Properties**

Asphalt binder or bitumen is a main ingredient in asphalt pavements along with aggregate and air voids (Lim et al., 2022). Asphalt is a viscoelastic petroleum derivative used in pavement construction and other construction applications (Karnati et al., 2019). Oxidative aging of asphalt pavement is one of the most common causes for pavement distresses (Karnati et al., 2019). Age hardening is a significant influence on the durability of asphalt pavement from undergoing oxidation which encourages pavement embrittlement (Karnati et al., 2019). Asphalt binder is composed of carbon, hydrogen, nitrogen, and sulfur (Lim et al., 2022). Service life of asphalt is mainly affected by aging, as it changes chemically due to varying temperatures and ultraviolet rays (Lim et al., 2022). Throughout the service life of asphalt binder there is a loss of light oil components, or maltenes, and an increased composition of heavy oil components, or asphaltenes (Zahoor et al., 2021). Deformations to asphalt occur as these asphaltene and maltene contents decline making the asphalt stiff and brittle (Lim et al., 2022). Effective quality control of asphalt binders extends the service life of asphalt (Lim et al., 2022). Current methods for testing quality
control are variable, using FTIR analysis is a more scientific approach that could provide better evaluations of quality control in asphalt binder mixed with various bio-based additives (Lim et al., 2022).

**Elemental Composition**

Elemental compositions of bio-based oils depend on the different biomass materials used (Zhang et al., 2020). By breaking down the percentages of carbon, hydrogen, oxygen, and nitrogen, there are distinct differences between bio-based oil and petroleum-based oil. There is a much higher oxygen element amount in bio-based oil than petroleum asphalt binder which is a reason for bio-based oils being prone to aging (Zhang, You, et al., 2021). This and the other elemental compositions vary with biomass sources which has shown major differences between swine waste-based and plant-based BO (Zhang, You, et al., 2021).

**Physical Properties**

The variability in BOs, or pyrolysis oils, and the lack of research creates contrasting results when its use in asphalt is studied. Some physical properties that are tested initially include penetration, softening point, ductility, and viscosity (Zhang et al., 2020). These aid in measuring the comparisons between bio-asphalts and petroleum-based asphalt binders. Studies have compared them and seen that BO content increased penetration into binder. There is penetration grade of 80/100 for asphalt (Zhang, You, et al., 2021). Softening point can provide information on the structure and molecular weight of the binder and is determined by when the asphalt binder retains a lower viscosity and softens under specific experimental conditions (Zhang, You, et al., 2021). Ductility is helpful for evaluating the plasticity of binder (Zhang, You, et al., 2021). The higher the ductility, the better the plasticity of binder and generally BOs have shown an improvement in the plasticity of asphalt (Zhang, You, et al., 2021). The penetration index
determines the sensitivity of the asphalt binder to temperature (Zhang, You, et al., 2021). WCO and BO used to modify asphalt binder has been generally found to increase penetration and ductility while lowering viscosity and softening point (Cao et al., 2019).

**FTIR**

FTIR analysis shows how molecules in a material structure absorb energy or radiation of a defined wavenumber (Lim et al., 2022). FTIR is a method used to obtain an infrared spectrum of absorption, emission, and photoconductivity of solid, liquid, and gas (Zhang, Han, et al., 2021). FTIR is used most frequently for the structural analysis and identification of compounds by showing varying wavelengths of radiation being absorbed which can be used to determine functional groups (Zhang, Han, et al., 2021). Infrared waves bounce off the material showing how much of those waves are transmitted or absorbed to identify different chemicals (Wang et al., 2020). Different wavenumbers and groups of them relate to these absorptions. IR spectra can be used to show compatibility between oils used in modifying asphalt binder (Wang et al., 2020). FTIR analysis also confirms that it is possible to determine if a binder has been modified or not (Lim et al., 2022). FTIR analysis constitutes a viable identification method for asphalt binders modified by additives for properties improvement (Lim et al., 2022). By studying the IR spectra, the chemical composition of bio-based oil is similar to that of asphalt showing feasibility for replacement of petroleum-based binder with bio-based oil (Wang et al., 2020). However, there are differences found between them that can affect their compatibility. Petroleum asphalt exhibits a large amount of C-H bending while wood-based BO has high S=O, C=O, and O-H stretching (Zhang, You, et al., 2021). When analyzing original binders, FTIR analysis shows peaks at wavenumbers of 2922 cm\(^{-1}\), 2853 cm\(^{-1}\), 1600 cm\(^{-1}\), 1460 cm\(^{-1}\), 1377 cm\(^{-1}\), and 813 cm\(^{-1}\) (Lim et al., 2022). Peaks around 1242 and 1739 cm\(^{-1}\) are related to C-H and C=O bonds and are
higher in bio-based oils (Lim et al., 2022). Oxygen containing functional groups are contributors to the aging of BO (Zhang, You, et al., 2021). FTIR tests are conducted to evaluate these bonds, specifically the C=O or carbonyl index of aged asphalt binder is used to determine aging effects (Lim et al., 2022). Different biomasses used in BO production along with these production and preparation methods can contribute to their effects on aging when used in asphalt binder (Zhang, You, et al., 2021). Petroleum asphalt binder is dominated by hydrocarbons whereas BO composition is much more complex (Zhang, You, et al., 2021). Between asphalt binders and BO modifiers these differences in complexity contribute to different properties, however some functional groups in sawdust BO were very similar to asphalt which could provide reason for compatibility in bio-asphalt production (Zhang, You, et al., 2021). A popular choice for BO production, wood-based or lignocellulosic biomasses are accessible and available as waste residues from a multitude of industries (Ali et al., 2015). FTIR analysis was completed on cotton stalk pyrolysis liquid showing peaks around 3353 cm\(^{-1}\) for O-H stretching and water content, 1700 cm\(^{-1}\) for C=O, and several others (Ali et al., 2015). The chemical structure shown through IR spectra of wood-based BO was more complicated with several additional peaks than when compared with WCO, BSFLO, and asphalt binders (Ali et al., 2015; Lim et al., 2022; Zozo et al., 2022).

Oxidative aging has been shown to cause changes in asphalt composition that make the material stiffer and prone to cracking (Cao et al., 2019). These changes in chemical properties impact asphalt rheology but are also detectable through FTIR (Cao et al., 2019). FTIR is a popular method to investigate changes in asphalt binder specifically the chemical composition due to oxidative aging (Hofko et al., 2018). FTIR has been used to monitor carbonyl and sulfoxide functional groups in asphalt binders before and after long-term aging (Karnati et al.,
By taking the area under the carbonyl band around 1700 cm$^{-1}$ the chemical aging indices can be calculated and used as reliable indicators of the extent of oxidative aging (Karnati et al., 2019). It has been documented that after oxidative aging both carbonyl (C=O) and sulfoxide (S=O) functional groups of asphalt binder increase (Karnati et al., 2019) (Hofko et al., 2018). However, pertaining to the S=O concentration in determining aging effects, some studies have shown negligible differences and should not be considered a reliable indicator to quantify this rate of aging (Arafat et al., 2020). After RTFOT aging one study showed no increase in the carbonyl area, however a distinct increase after PAV aging (Hofko et al., 2018). The increase of the carbonyl peak and area is a relative indicator of oxidation while the peak is not an absolute indicator of oxidation (Hofko et al., 2018).

In one study the IR spectra recorded no significant impact from RTFOT temperatures on short term and long-term aged materials regardless of the temperature used for RTFOT (Hofko et al., 2018). While in this same study short-term aging temperature did not affect the samples carbonyl index in long-term aging, differences between unaged and PAV aged samples were significant (Hofko et al., 2018). Moreover, using the FTIR method different binder sources could be detected (Hofko et al., 2018). FTIR spectra of whole BSFLO samples have been studied revealing peaks around 1650 cm$^{-1}$ that represent high concentrations of carbonyl groups and of C-H bonds (Zozo et al., 2022).

**Rheological Properties**

Asphalt binder is a viscoelastic material which shows different behaviors at different temperatures (Karnati et al., 2019). Therefore, rheological properties of bio-asphalt, which are how deformation and flow behaviors respond to stresses, are evaluated at high-temperature, intermediate temperature, and low-temperature (Zhang et al., 2020). Overall, bio-based oil
Modification decreases asphalt binder stiffness across all temperature ranges which improves low-temperature performance and fatigue performance while decreasing high-temperature performance grade (Lei et al., 2017). Dynamic shear rheometers (DSR) are used to determine rheological properties of asphalt binders and aided in the grading of high-temperature performance (Lei et al., 2017). Studies have shown that bio-based oils can be used as rejuvenators to restore rheological properties of aged binders as well (Cao et al., 2019).

Mixability and workability strongly correlate with the viscosity or flow of the binder (Zhang, You, et al., 2021). Viscosity measurements investigate the resistance to flow and the workability of asphalt (Zhang, R. et al., 2018). Achieving higher viscosities at high temperatures is ideal (Wang et al., 2012). However, too high viscosity may contribute to thermal cracking of asphalt binder at low temperatures while too low viscosity causes negative effects at high temperatures (Zhang, You, et al., 2021). Bio-based oils in asphalt binder are generally found to lower viscosity (Cao et al., 2019). One study used test temperatures of 110°C, 135°C, 150°C and 165°C, and a shear rate of 20 rotations per minute (Zhang, R. et al., 2018). In the same study viscosities of all asphalt binders decreased with the increase of temperature (Zhang, R. et al., 2018). Aging causes the asphalt to become rigid and viscous while bio-rejuvenator can help reduce the viscosity of the asphalt binder to some extent (Zhang, R. et al., 2018). Some bio-based oils will exhibit characteristics of shear thinning, which explains that the viscosity depends on the shear rate (Uchoa et al., 2021). Pseudoplastic is another name for this behavior (Uchoa et al., 2021). Generally, there is a higher viscosity at low shear rates (Uchoa et al., 2021). In one study, using spindle SC4-21 at 20 rotations per minute demonstrated an expected decrease in viscosity with an increase in temperature (Uchoa et al., 2021). Increasing bio-additives can create significantly higher viscosity (Uchoa et al., 2021). Related to asphalt binder being a viscoelastic
material, rutting happens at high temperature, fatigue cracking at intermediate temperature, and thermal cracking at low temperature (Zhang, You, et al., 2021).

**Rutting Resistance at High Temperature**

One of the biggest concerns with modifying asphalt binders with bio-based oils is their effect on high-temperature performance due to the decrease in stiffness which causes rutting or depressions in pavement (Lei et al., 2017). The addition of bio-based oils tends to negatively affect the high-temperature performance of asphalt binder (Lei et al., 2017). The multiple stress creep recovery test (MSCR) is used to ascertain the rutting resistance of asphalt binders (Lei et al., 2017). This will show the optimum oil content for most rutting resistance in asphalt binders at high temperatures and pressures (Lei et al., 2017). The addition of bio-based oils generally increases rutting which occurs at high temperatures (Cao et al., 2019). However, biomass inputs can affect these results for example, swine manure-based bio-asphalt has been found to have the best rutting resistance when compared to other BOs like wood BO-based bio-asphalt which has shown the lowest rutting resistance (Zhang, You, et al., 2021).

**Fatigue Resistance at Intermediate Temperature**

The linear amplitude sweep (LAS) test helps characterize asphalt fatigue performance and the real damage resistance of asphalt (Lei et al., 2017). The results of one study showed an improvement in fatigue and damage tolerance after oil modifiers were added (Lei et al., 2017). Bio-based oils are generally found to improve cracking resistance at intermediate and low temperatures (Cao et al., 2019).

**Thermal Cracking at Low Temperature**

Studies have used the bending beam rheometer (BBR) test to evaluate low-temperature performance of asphalt binders modified with bio-based oils (Lei et al., 2017). Stiffness and
relaxation rate can be measured (Lei et al., 2017). A linear correlation between decrease in stiffness and increase in relaxation rate with increase in bio-based oil content are beneficial relationships for low-temperature performance of asphalt binder (Lei et al., 2017).

**Anti-Aging Properties**

Aging resistance is a large concern with bio-based modified asphalt due to the excellent service performance of conventional asphalt pavement (Zhang et al., 2020). Short-term and long-term aging of asphalt binders has been evaluated using a RTFOT and a PAV (Lei et al., 2017). Short-term aging through RTFOT simulates storage and construction conditions for asphalt while long-term aging with a PAV simulates service life (Lei et al., 2017). BO from sawdust showed an increase in the complex shear modulus of asphalt binder at the same frequency conditions after RTFOT. This is desirable for the prevention of rutting in asphalt mixtures (Gao et al., 2018). The addition of BO could increase the anti-deformation ability of asphalt after RTFOT (Gao et al., 2018). Different effects on the aging resistance of aged asphalt can be found using different kinds of bio-based oils (Zhang et al., 2020).

**ASTM Standard Test Methods for Asphalt Binder**

The American Society for Testing and Materials (ASTM) develops technical standards for a wide range of services including asphalt binder. RTFOT is a standard test method for the effect of heat and air, and mimics conventional hot mixing of asphalt at about 150℃ (ASTM Standard D2872, 2022). Other studies of heat and air effects on binder use temperatures between 123℃ to 163℃ for 30 minutes in RTFOT (Hofko et al., 2018). Varying this temperature will have a more or less effect on asphalt properties (ASTM Standard D2872, 2022). Pressurized aging vessels (PAV) simulate the oxidative aging that occurs during the service life of asphalt
binders (ASTM Standard D6521, 2022). PAV method is completed at a temperature of 100°C with an air pressure of 2.1 MPa for 20 hours (Hofko et al., 2018).

**Methodology**

**Introduction**

In this study BSFL will be compared on a functional basis against asphalt binder, or the conventional material used in the asphalt industry. Asphalt binder, or distilled petroleum will stand as the control.

**Sample Descriptions**

The BO product used in this study is BSFL, labeled BSF and called EnviroOil from EnviroFlight, which is shown in Figure 1 (2022). The oil used in this study is 98% dried BSFL and 2% water and BSFL meal solids with less than 1% insoluble impurities (EnviroFlight, 2022). The controls are two asphalt binders from Associated Asphalt Salisbury LLC distilled from petroleum and rated for different temperatures. The samples, labels, and descriptions can be found in Table 1. The control sample labeled 64CO is an asphalt binder performance graded (PG) at 64-22 which is rated to the temperature of an area and can handle a low of -22°C and high of 64°C. The other asphalt binder labeled 70CO is PG 70-22 or graded for a low of -22°C and a high of 70°C. Both binders were pulled from production in October of 2021.
Sample Preparations

For the experiment multiple samples were created using the PG 70-22 and the PG 64-22 asphalt binder as the bases. Each of the modified asphalt binders, or bio-asphalts, will have different percentages of BSFLO. Each asphalt binder will have either 5, 10, or 20% by weight of BSFLO mixed in. In total there are 3 samples of each of the 12 samples of bio-asphalts along with the controls of each asphalt binder, PG 70-22, and PG 64-22. Including the controls and BSFLO themselves there are 45 samples and 42 of them will undergo aging for 48 hours and then again for 48 more hours or 96 hours total at 110°C. Without RTFOT or PAV equipment aging duration and temperature were chosen with only oxidative aging effects in mind using a
lower temperature, but longer duration chosen than ASTM standard testing conditions for RTFOT and PAV. This study is for discovering foundational results of the impact on oxidative aging with the use of BSFLO in bio-asphalt.

When preparing the samples each one was separately heated and kept in an oven at 110°C for one to two hours to lower viscosity and make pouring easier. The BSFLO was heated in the oven for only 25 minutes, shown in Figure 1, due to reaching a lower viscosity more quickly. An aluminum can is weighed to subtract from the approximately 200 grams of each asphalt binder that is weighed into 42 cans. Each weight of the asphalt binder is then multiplied by the percentage of bio-based oil desired for each sample as shown in Equation 1. Then using a Thermo Scientific stirring hot plate, shown in Figure 2, each of these samples were kept at a temperature range of 200°C to 240°C as it was mixed at 1100 rotations per minute (rpm) for 30 minutes. Over the several hours of mixing samples, the combined samples that had not been mixed were kept in the oven at 110°C for one to three hours each. Preparation parameters of bio-asphalts are shown in Table 2. For each sample listed in Table 1 there are three of each sample to increase precision during experimental FTIR testing. Moreover, three to ten grams of each of the three samples for each sample group was then poured into three aluminum two-ounce containers, shown in Figure 3, for FTIR testing before aging and after aging for 48 and 96 hours at 110°C.

\[
\text{Weight of Asphalt Binder} \times \text{Desired Percentage} = \text{Weight of BO Added} \tag{1}
\]
### Table 1

**Sample Descriptions**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Label</th>
<th>Origin</th>
<th>Description (at room temperature)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSFLO</td>
<td>BSFLO</td>
<td>EnviroOil</td>
<td>A yellowy-brown colored, semi-solid BO</td>
</tr>
<tr>
<td>PG 64-22 Asphalt Binder</td>
<td>64CO</td>
<td>Associated Asphalt Salisbury LLC</td>
<td>A black thick solid petroleum-based oil</td>
</tr>
<tr>
<td>PG 70-22 Asphalt Binder</td>
<td>70CO</td>
<td>Associated Asphalt Salisbury LLC</td>
<td>A black thick solid petroleum-based oil</td>
</tr>
<tr>
<td>5% BSF with 70CO</td>
<td>70-5BSF</td>
<td>Lab created</td>
<td>A black, solid mixture of 5% BSFL BO with PG 70-22 asphalt binder</td>
</tr>
<tr>
<td>10% BSF with 70CO</td>
<td>70-10BSF</td>
<td>Lab created</td>
<td>A black, solid mixture of 10% BSFL BO with PG 70-22 asphalt binder</td>
</tr>
<tr>
<td>20% BSF with 70CO</td>
<td>70-20BSF</td>
<td>Lab created</td>
<td>A black, solid mixture of 20% BSFL BO with PG 70-22 asphalt binder</td>
</tr>
<tr>
<td>5% BSF with 64CO</td>
<td>64-5BSF</td>
<td>Lab created</td>
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</tr>
<tr>
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<td>64-10BSF</td>
<td>Lab created</td>
<td>A black, solid mixture of 10% BSFL BO with PG 64-22 asphalt binder</td>
</tr>
<tr>
<td>20% BSF with 64CO</td>
<td>64-20BSF</td>
<td>Lab created</td>
<td>A black, solid mixture of 20% BSFL BO with PG 64-22 asphalt binder</td>
</tr>
</tbody>
</table>

### Table 2

**Preparation Parameters of Bio-Asphalts**

<table>
<thead>
<tr>
<th>Asphalt Binder Sample (g)</th>
<th>Container Weight (g)</th>
<th>BO (%)</th>
<th>BO (g)</th>
<th>Shearing Temperature (°C)</th>
<th>Shearing Viscosity (RPM)</th>
<th>Shearing Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>~150-200</td>
<td>~50-85</td>
<td>BO (g)</td>
<td>3, 5, or 10% of asphalt binder controls by weight</td>
<td>200-240</td>
<td>1100</td>
<td>30</td>
</tr>
</tbody>
</table>
Note. The thermos scientific hot plate is shown being used to mix the 64-10BSF bio-asphalt at 239°C and 1100 rpm for 30 minutes.
Figure 3

Asphalt Binder and Bio-Asphalt Samples Experiencing Aging

Note. Asphalt binder and bio-asphalt samples in aluminum two-ounce containers experiencing aging at 110°C.
FTIR Test

To compare these oils in terms understood by current scientific research on BO use in asphalt binder, the analytical technique FTIR testing was used to characterize functional groups. The data acquisition procedures and instrumentation in FTIR testing is described.

Chemical properties of modified asphalt binder can be shown by FTIR. To provide an analysis of the C=O functional group in these samples a FTIR test of the BSF, 70CO, and 64CO oils were run by themselves. After preparing the 36 bio-asphalts modified with BSFLO, an FTIR test was run on them as well. Each result obtained from the FTIR testing was calculated using the average spectra of the IR spectra of each of the three samples of each asphalt binder and bio-asphalt allowing for determination of significant differences between samples. This was completed for each bio-asphalt in each FTIR test for the two aging durations.

In this study the Nicolet 6700 device from Thermo Scientific located in the spectroscopy lab of the chemistry department at Appalachian State University was used in all experiments. The range of 4000-400 cm\(^{-1}\) was used. Samples were directly attached to the diamond surface of the device which shows attenuated total reflectance (ATR). ATR when applied is unaffected by the shape and color of the samples measured (Lim et al., 2022). Acetone was used to clean the surface of any residual contribution from previous samples.

The initial FTIR tests will then be compared to the future ones after aging. After aging is completed at 110°C for 48 hours on all 36 bio-asphalts and 6 asphalt binder control samples a second FTIR test is run. After aging again at 110°C for 48 hours, which is a total of 96 hours, a third FTIR test is run.
**Question 1 Methods**

By examining the IR spectra of original asphalt binder samples, BSFLO, and bio-asphalts, specifically in the carbonyl index region of 1850-1650 cm⁻¹ showing carbonyl concentration, differences in sample carbonyl indexes could show differences between asphalt binders and bio-asphalts.

**Question 2 Methods**

By calculating the area under the curve from 1850-1650 cm⁻¹ for all samples including the unaged and then aged by 48 hours and 96 hours, the aging effects on the potential performance of asphalt could be demonstrated. To calculate the area under the curve for each sample Equation 2 was used on x and y coordinates between 1850-1650 cm⁻¹. The last coordinate for 1850 cm⁻¹ was deleted to ensure that the area past these values was not included. Then the areas calculated from 1850-1650 cm⁻¹ were summed to provide overall area for each sample.

\[
\sum_{i=0}^{n} \frac{(y_1+y_2)}{2(x_2-x_1)} = \text{Area Under Curve}
\]  

(2)

**Question 3 Methods**

By comparing the areas under the C=O concentration curve from 1850-1650 cm⁻¹ for each sample it could be determined if there were significant differences between unaged and aged samples. Oxidative aging is proportional to an increasing C=O concentration. Likewise aging resistance is inversely proportional to increasing C=O concentration. The greater the aging resistance the lesser the C=O concentration and therefore less area under the curve from 1850-1650 cm⁻¹ as shown in Equation 3.

\[
\text{Aging Resistance} \propto \frac{1}{\text{C=O Stretching}}
\]  

(3)
Question 4 Methods

By comparing the carbonyl index or C=O concentration between unaged and aged samples of asphalt binder with that of bio-asphalts the differences in aging resistances for these samples show how BSFLO affects aging resistance in asphalt binder. If C=O concentration is significantly decreased in BSFLO modified bio-asphalts compared to C=O concentration in petroleum-based asphalt binder, then it could be concluded that BSFLO could have a positive effect by increasing aging resistance in asphalt binder. A two-tailed t-test assuming unequal variances was used to indicate significant difference and the significance threshold was set at .05.

Data Analysis and Results

Understanding Variability

Baseline Variability

Before every FTIR testing session, background samples are taken to decrease variability in sample IR spectra due to variance in the air surrounding the equipment. Background sampling should decrease variability in sample IR spectra however baseline test runs without any samples present show small amounts of absorbance still occurring. The absorbance of the air is shown in Figure 4 demonstrating slight variability specifically in the lowest wavelengths or the fingerprint region. These variabilities being below 0.2 are negligible especially for the region of C=O concentration, as they effect different wavenumbers than 1850-1650 cm\(^{-1}\).
Figure 4

*FTIR Spectra of Baseline*

Note. The absorbances of the air with no samples present are demonstrated.

**Testing Room Variability**

Another possible variability came from carbon dioxide levels. To show the possible variability, the IR spectra for original bio-asphalts were used. The zoom plot of 2500-2200 cm\(^{-1}\) within Figure 5 is an example of how carbon dioxide coming from respiration inside the room affects the FTIR results.
Figure 5

Possible Testing Room Variability in FTIR Spectra of Bio-Asphalt Samples

Note. Within the IR spectra of original bio-asphalt samples the possible area affected by respiring carbon dioxide in the testing room is seen in the zoom plot.

*Wood-Based BO Variability*

Wood-based BO results were excluded from data analysis and results due to large standard deviations in IR spectra in samples. The first set of results for wood-based BO was taken from the transmittance graphs instead of the absorbance graphs. Through calculations data was skewed and therefore excluded. The standard deviations of all the samples are shown in
Table 3. Specifically, the maximum and average SD for 70-5HW, 70-10HW, 64-5HW, and 64-10HW were drastically higher than the BSF modified asphalt binders.

Table 3

Maximum and Average Standard Deviation (SD) for All Samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Maximum SD</th>
<th>Average SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline</td>
<td>3.40</td>
<td>1.58</td>
</tr>
<tr>
<td>70CO</td>
<td>0.10</td>
<td>0.00</td>
</tr>
<tr>
<td>70CO-48</td>
<td>0.22</td>
<td>0.03</td>
</tr>
<tr>
<td>70CO-96</td>
<td>0.25</td>
<td>0.01</td>
</tr>
<tr>
<td>64CO</td>
<td>0.11</td>
<td>0.01</td>
</tr>
<tr>
<td>64CO-48</td>
<td>0.06</td>
<td>0.01</td>
</tr>
<tr>
<td>64CO-96</td>
<td>0.07</td>
<td>0.01</td>
</tr>
<tr>
<td>70-5BSF</td>
<td>0.10</td>
<td>0.01</td>
</tr>
<tr>
<td>70-10BSF</td>
<td>0.10</td>
<td>0.01</td>
</tr>
<tr>
<td>70-20BSF</td>
<td>0.09</td>
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</tr>
<tr>
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</tr>
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Table 4 Continued

Maximum and Average Standard Deviation (SD) for All Samples

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<th>Sample</th>
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<th>Average SD</th>
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<td>70-10HW-96</td>
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<td>0.02</td>
</tr>
<tr>
<td>70-20HW-96</td>
<td>0.12</td>
<td>0.02</td>
</tr>
<tr>
<td>64-5HW-96</td>
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<td>0.02</td>
</tr>
<tr>
<td>64-10HW-96</td>
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</tr>
<tr>
<td>64-20HW-96</td>
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<td>0.03</td>
</tr>
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</table>

Question 1 Results

An FTIR test was conducted on all samples before any aging was completed. This includes three samples of each asphalt binder control, three samples of the BSFLO, and the three of each of the 12 bio-asphalt samples. In Figures 6, 7, and 8 there are two distinct peaks that distinguish BSFLO from the controls which are the peaks shown at 1750 cm\(^{-1}\), which is indicative of C=O concentration, and 1150 cm\(^{-1}\) indicative of C-H bonds. These peaks in the IR spectra of BSFLO and not for PG 64-22 or PG 70-22 create metrics for determining whether the asphalt binder has been modified by BSFLO in the bio-asphalt samples.

This is further proven by Figures 9-17 showing that as the percentage of BSFLO in the bio-asphalt samples increases so do the peaks at 1750 cm\(^{-1}\) and at 1150 cm\(^{-1}\). Figure 18 shows that within the IR spectra there are increasing C=O concentrations with the increase in percentage of BSFLO added to the PG 70-22 and PG 64-22 asphalt binders. FTIR can be used to distinguish modifiers in asphalt binders. Figures 20, 21 and 22 demonstrate that there are no significant differences between the two asphalt binders, PG 70-22, and PG 64-22, so, distinguishing between these using FTIR even after aging is unavailable.
Note. The average absorbances of the unaged original samples of BSFLO, 70CO, and 64CO are shown.
Figure 7

Zoom Plot of 1850-1650 cm\(^{-1}\) in IR Spectra of Original Samples

Note. The average absorbances of the unaged original samples of BSFLO, 70CO, and 64CO are shown in wavenumbers 1850-1650 cm\(^{-1}\).
Note. The average absorbances of the unaged original samples of BSFLO, 70CO, and 64CO are shown in wavenumbers 1250-1050 cm$^{-1}$. 

Figure 8

Zoom Plot of 1250-1050 cm$^{-1}$ in IR Spectra of Original Samples
**Figure 9**

*FTIR Spectra of 70-BSF Bio-Asphalt Samples*

![FTIR Spectra of 70-BSF Bio-Asphalt Samples](image)

*Note.* The average absorbances of the unaged bio-asphalt samples of 70-5BSF, 70-10BSF, and 70-20BSF are shown.
Figure 10

*Zoom Plot of 1850-1650 cm$^{-1}$ in IR Spectra of 70-BSF Bio-Asphalt Samples*

*Note.* The average absorbances of the unaged bio-asphalt samples of 70-5BSF, 70-10BSF, and 70-20BSF are shown in wavenumbers 1850-1650 cm$^{-1}$. 
Figure 11

*Zoom Plot of 1250-1050 cm\(^{-1}\) in IR Spectra of 70-BSF Bio-Asphalt Samples*

*Note.* The average absorbances of the unaged bio-asphalt samples of 70-5BSF, 70-10BSF, and 70-20BSF are shown in wavenumbers 1250-1050 cm\(^{-1}\).
**Figure 12**

*FTIR Spectra of 64-BSF Bio-Asphalt Samples*

*Note.* The average absorbances of the unaged bio-asphalt samples of 64-5BSF, 64-10BSF, and 64-20BSF are shown.
Figure 13

*Zoom plot of 1850-1650 cm\(^{-1}\) in IR Spectra of 64-BSF Bio-Asphalt Samples*

*Note.* The average absorbances of the unaged bio-asphalt samples of 64-5BSF, 64-10BSF, and 64-20BSF are shown in wavenumbers 1850-1650 cm\(^{-1}\).*
Figure 14

Zoom plot of 1250-1050 cm\(^{-1}\) in IR Spectra of 64-BSF Bio-Asphalt Samples

Note. The average absorbances of the unaged bio-asphalt samples of 64-5BSF, 64-10BSF, and 64-20BSF are shown in wavenumbers 1250-1050 cm\(^{-1}\).
Figure 15

FTIR Spectra of Asphalt Binders and 64- and 70-BSF Bio-Asphalt Samples

Note. The average absorbances of the unaged bio-asphalt samples of 70CO, 64CO, 70-5BSF, 70-10BSF, 70-20BSF, 64-5BSF, 64-10BSF, and 64-20BSF are shown.
Figure 16

Zoom plot of 1850-1650 cm\(^{-1}\) in IR Spectra of Asphalt Binders and 64- and 70-BSF Bio-Asphalt Samples

Note. The average absorbances of the unaged bio-asphalt samples of 70CO, 64CO, 70-5BSF, 70-10BSF, 70-20BSF, 64-5BSF, 64-10BSF, and 64-20BSF are shown in wavenumbers 1850-1650 cm\(^{-1}\).
Figure 17

Zoom plot of 1250-1050 cm\(^{-1}\) in IR Spectra of Asphalt Binders and 64- and 70-BSF Bio-Asphalt Samples

Note. The average absorbances of the unaged bio-asphalt samples of 70CO, 64CO, 70-5BSF, 70-10BSF, 70-20BSF, 64-5BSF, 64-10BSF, and 64-20BSF are shown in wavenumbers 1250-1050 cm\(^{-1}\).
Figure 18

Areas of Carbonyl Index for Unaged Samples

Note. The mean area of carbonyl index for the unaged controls and original bio-asphalt samples, error bars show standard deviation above and below each mean area.

Question 2 Results

The areas under the curves demonstrating the carbonyl index were calculated and compared between all aged and unaged samples. Based on the results shown in Figure 19 there are trends of increasing C=O concentration as aging advances. The 64CO samples had a high carbonyl index before aging. This also effected the comparison of the 64CO samples before and after 48 hours of aging showing a lower carbonyl index than it did before aging. This does not correlate with the trend for the rest of the samples stated above and could be related to the number of samples and their effect on precision. There are greater amounts of C=O concentration for higher amounts of BSFLO before aging. However, the C=O areas in all
samples after 48 hours and 96 hours are not significantly different. This shows that the controls had quicker accumulations of C=O concentrations than the bio-asphalts to reach the same level of C=O concentrations after 96 hours of aging. This could indicate that BSFLO modification does not affect aging susceptibility in comparison to the controls or asphalt binders.

**Figure 19**

*Areas of Carbonyl Index for Unaged and Aged Samples*

![Areas of Carbonyl Index for Unaged and Aged Samples](image)

*Note.* Within the IR spectra of the unaged and aged controls and bio-asphalt samples the area of the carbonyl index was determined, including the standard deviation above and below each mean area shown in the error bars.
Question 3 Results

There are changes and differences between asphalt binders and bio-asphalts as they underwent aging. In Figures 20, 21, and 22, there are no significant differences between the PG 70-22 and PG 64-22 asphalt binders throughout aging (p > .05). In Table 4 the p values between unaged samples and samples aged for 48 hours showed no significant differences (p > .05). In Figures 23, 24, and 25, there are no significant differences after 96 hours of aging between PG 70-22 asphalt binder and all BSFLO modified bio-asphalts with PG 70-22 (p > .05). In Figures 26, 27, and 28, there are no significant differences after 96 hours of aging between PG 64-22 asphalt binder and all BSFLO modified bio-asphalts with PG 64-22. In Figures 29, 30, 31, 33, and 36, there are significant differences between unaged samples and samples aged for 96 hours showing that FTIR can demonstrate these differences, but as seen in Table 4 it cannot demonstrate differences for samples aged for 48 hours.

Figure 20

Two-Tailed T-Test of Carbonyl Index for Unaged 70CO and 64CO Samples (p=.25)
Note. The mean area of carbonyl index for unaged 70CO and 64CO samples, differences significant at the $p < .05$ level, error bars show standard deviation above and below each mean area.

Figure 21

Two-Tailed $T$-Test of Carbonyl Index for 70CO and 64CO Samples Aged for 48 Hours ($p=.43$)

Note. The mean area of carbonyl index for 70CO and 64CO samples after 48 hours of aging, differences significant at the $p < .05$ level, error bars show standard deviation above and below each mean area.
Note. The mean area of carbonyl index for 70CO and 64CO samples after 96 hours of aging, differences significant at the $p < .05$ level, error bars show standard deviation above and below each mean area.
Table 5

*P Values from Two-Tailed T-Tests of Carbonyl Index for Unaged Samples and Samples Aged for 48 Hours*

<table>
<thead>
<tr>
<th>Samples</th>
<th>p Values</th>
<th>Standard Deviation for Unaged Samples (above and below each mean C=O area)</th>
<th>Standard Deviation for Samples Aged for 48 Hours (above and below each mean C=O area)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70CO</td>
<td>.44</td>
<td>.41</td>
<td>2.9</td>
</tr>
<tr>
<td>64CO</td>
<td>.41</td>
<td>.78</td>
<td>1.2</td>
</tr>
<tr>
<td>70-5BSF</td>
<td>.11</td>
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<td>.99</td>
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<td>.56</td>
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<td>.49</td>
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<td>.64</td>
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</tr>
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<tr>
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</tbody>
</table>

*p < .05.
Figure 23

Two-Tailed T-Test of Carbonyl Index for 70CO and 70-5BSF Samples Aged for 96 Hours

(p = .23)

Note. The mean area of carbonyl index for 70CO and 70-5BSF samples after 96 hours of aging, differences significant at the p < .05 level, error bars show standard deviation above and below each mean area.
Figure 24

Two-Tailed T-Test of Carbonyl Index for 70CO and 70-10BSF Samples Aged for 96 Hours

\(p=.45\)

Note. The mean area of carbonyl index for 70CO and 70-10BSF samples after 96 hours of aging, differences significant at the \(p < .05\) level, error bars show standard deviation above and below each mean area.
Figure 25

Two-Tailed T-Test of Carbonyl Index for 70CO and 70-20BSF Samples Aged for 96 Hours

(p=.81)

Note. The mean area of carbonyl index for 70CO and 70-20BSF samples after 96 hours of aging, differences significant at the p < .05 level, error bars show standard deviation above and below each mean area.
Figure 26

Two-Tailed T-Test of Carbonyl Index for 64CO and 64-5BSF Samples Aged for 96 Hours

(p=.40)

Note. The mean area of carbonyl index for 64CO and 64-5BSF samples after 96 hours of aging, differences significant at the p < .05 level, error bars show standard deviation above and below each mean area.
Figure 27

Two-Tailed T-Test of Carbonyl Index for 64CO and 64-10BSF Samples Aged for 96 Hours

\( (p = .67) \)

Note. The mean area of carbonyl index for 64CO and 64-10BSF samples after 96 hours of aging, differences significant at the \( p < .05 \) level, error bars show standard deviation above and below each mean area.
Figure 28

**Two-Tailed T-Test of Carbonyl Index for 64CO and 64-20BSF Samples Aged for 96 Hours**

\[(p = .93)\]

![Graph showing mean carbonyl index for 64CO and 64-20BSF samples after 96 hours of aging.](image)

*Note.* The mean area of carbonyl index for 64CO and 64-20BSF samples after 96 hours of aging, differences significant at the \( p < .05 \) level, error bars show standard deviation above and below each mean area.

**Question 4 Results**

The aging caused by exposure to 110°C for 96 hours is statistically significant and shown in the \( p \) values from the t-tests for 70CO, 64CO, 70-5BSF, 70-20BSF, and 64-20BSF are numbers under .05, shown in Figures 29, 30, 31, 33, and 36. Samples 70-10BSF, 64-5BSF, and 64-10BSF did not show significant differences between unaged and aged samples shown in Figures 32, 34, and 35 \((p > .05)\). There is a possibility that since these three BSFL bio-asphalt samples were not significantly different through aging that the addition of BSFLO could slow
Aging. Aging caused significant differences between most samples. However, when comparing asphalt binders and bio-asphalts after 96 hours of aging at 110℃ there are no significant differences (Figures 23-28) so, BSFLO could potentially be used in asphalt binder with no effect on aging resistance.

**Figure 29**

*Two-Tailed T-Test of Carbonyl Index for Unaged 70CO and 70CO Aged for 96 Hours Samples (p < .01)*

*Note.* The mean area of carbonyl index for unaged 70CO and 70CO aged for 96 hours samples, differences significant at the p < .05 level, error bars show standard deviation above and below each mean area.
Figure 30

Two-Tailed T-Test of Carbonyl Index for Unaged 64CO and 64CO Aged for 96 Hours Samples

\( p = .04 \)

Note. The mean area of carbonyl index for unaged 64CO and 64CO aged for 96 hours samples, differences significant at the \( p < .05 \) level, error bars show standard deviation above and below each mean area.
Figure 31

Two-Tailed T-Test of Carbonyl Index for Unaged 70-5BSF and 70-5BSF Aged for 96 Hours Samples (p=.03)

Note. The mean area of carbonyl index for unaged 70-5BSF and 70-5BSF aged for 96 hours samples, differences significant at the p < .05 level, error bars show standard deviation above and below each mean area.
Figure 32

Two-Tailed T-Test of Carbonyl Index for Unaged 70-10BSF and 70-10BSF Aged for 96 Hours 
Samples (p=.06)

Note. The mean area of carbonyl index for unaged 70-10BSF and 70-10BSF aged for 96 hours samples, differences significant at the p < .05 level, error bars show standard deviation above and below each mean area.
Figure 33

*Two-Tailed T-Test of Carbonyl Index for Unaged 70-20BSF and 70-20BSF Aged for 96 Hours Samples (p=.04)*

*Note.* The mean area of carbonyl index for unaged 70-20BSF and 70-20BSF aged for 96 hours samples, differences significant at the $p < .05$ level, error bars show standard deviation above and below each mean area.
Figure 34

Two-Tailed T-Test of Carbonyl Index for Unaged 64-5BSF and 64-5BSF Aged for 96 Hours

Samples (p=.06)

Note. The mean area of carbonyl index for unaged 64-5BSF and 64-5BSF aged for 96 hours samples, differences significant at the p < .05 level, error bars show standard deviation above and below each mean area.
Figure 35

Two-Tailed T-Test of Carbonyl Index for Unaged 64-10BSF and 64-10BSF Aged for 96 Hours Samples (p=.07)

Note. The mean area of carbonyl index for unaged 64-10BSF and 64-10BSF aged for 96 hours samples, differences significant at the p < .05 level, error bars show standard deviation above and below each mean area.
Figure 36

Two-Tailed T-Test of Carbonyl Index for Unaged 64-20BSF and 64-20BSF Aged for 96 Hours Samples (p=.04)

*Note.* The mean area of carbonyl index for unaged 64-20BSF and 64-20BSF aged for 96 hours samples, differences significant at the p < .05 level, error bars show standard deviation above and below each mean area.

**Discussions and Future Research**

In the following sections the summary of outcomes in this study along with future recommendations and discussions are covered. Using the samples created for this work, further analysis of bio-asphalt should be conducted using ASTM standard methods and tests. The potential of BSFLO in bio-asphalt production is promising as shown in the lack of difference in susceptibility to aging with the addition of the oil.
Carbonyl index in FTIR can show differences between asphalt binders and BSFL bio-asphalt and is linked with aging susceptibility of these materials as seen in the literature and results (Zhang, You, et al., 2021; Lim et al., 2022). However, the few bio-asphalts that did not have significant differences between unaged and aged samples of 70-10BSF, 64-5BSF, and 64-10BSF, shown in Figures 32, 34, and 35, with p values greater than .05, could have had significant differences with more samples. This could also point to a slower aging effect found in BSFLO modified samples. It is interesting to note that even though the initially higher C=O concentration can mean decreased aging resistance, the BSFLO modified asphalt binder had similar aging behavior as the petroleum-based controls did. In Figure 19, unaged 70-20BSF and 64-20BSF samples have a higher carbonyl index compared to the unaged controls however, after 96 hours of aging they have no significant differences meaning almost equal areas of C=O concentrations, shown in Figures 23-28 (Zhang et al., 2020; Cao et al., 2019). The total increase in C=O concentration from unaged to aged samples is less for the BSFLO modified asphalt than the controls. BSFLO, in small percentages, could be added to asphalt binder without negatively affecting the aging resistance. Further testing is required to determine optimum percentage of BSFLO modification.

By comparing the IR spectra of petroleum asphalt binder to different bio-based oils, finding similarities in functional groups could point to more compatibility between oils (Zhang, You, et al., 2021). Very similar peaks were seen at 2920 cm\(^{-1}\), 2850 cm\(^{-1}\), 1450 cm\(^{-1}\), and 1370 cm\(^{-1}\) between the petroleum-based asphalt binder and the BSFLO as seen in Figure 15. This is very promising for their compatibility especially when seeing the complexity in wood-based BO shown in Figure 26. BSFLO has two other major peaks apart from the asphalt binders at 1750 cm\(^{-1}\) representing the higher carbonyl index (Figure 16) and 1150 cm\(^{-1}\) indicative of C-H bonds
(Figure 17). Compared to the various unmatched peaks of the wood-based BO, BSFLO shows strong compatibility with petroleum asphalt binder. As shown in Figures 6, 7, 8, and 26 BSFLO has main differences around C=O and C-H stretching however most other functional groups are very similar. Even though wood-based BO data was excluded from the results due to high standard deviations between samples as seen in Table 3, in Figure 37 the overall IR spectra is shown for all original samples including the wood-based BO labeled HW BO. Experimental breakdowns in Appendix A include HW BO samples. HW BO sample descriptions can be found in Appendix B. The feasibility for replacing petroleum-based binders with bio-based oils can be determined by studying the IR spectra to show similar chemical compositions between the oils (Wang et al., 2020). When looking at Figure 37 and the IR spectra of the original samples, HW BO or the wood-based BO is much more complex than the BSFLO and the asphalt binders and shows less compatibility in terms of similar chemical structures with asphalt binders than BSFLO.

When comparing the effects of bio-based oils converted from different biomass sources in different ways, there have been varying results. Overall, a reduction in high-temperature qualities has been seen in BO, or pyrolysis oil, modified binders with a better aging resistance found in animal-based bio-asphalts, such as with swine manure, than in plant-based bio-asphalts, such as with wood-based (Zhang, You, et al., 2021). It does depend on the biomass source however, overall performances of bio-based asphalt binders showed a negative impact on high-temperature performance and a positive impact on low-temperature performance (Zhang, You, et al., 2021). Even with a slight decrease in high-temperature stability of aged asphalt, BO can still improve aging resistance (Zhang et al., 2020). On the other hand, oils produced through mechanical processes such as animal and vegetable WCOs have been seen to reinstate basic
properties in aged asphalt binder (Zahoor et al., 2021). Researchers have agreed that waste vegetable oil can aid in thermal cracking resistance and reduced viscosity in asphalt binder (Khedaywi & Melhem, 2022). BSFLO has a similar chemical structure to cooking oils and again, as seen in Figure 37, BSFLO could have potential in bio-asphalt production and aged asphalt rejuvenation more so than the more chemically complicated wood-based pyrolysis oil (Zahoor et al., 2021; Zozo et al., 2022).

When calculating and examining the sulfoxide (S=O) concentration in these asphalt binders there were negligible differences in unaged and aged samples. Previous studies show an increase in both C=O and S=O concentration due to aging, however, S=O concentrations were negligible in this study (Arafat et al., 2020). There is hardly any study available where the aging susceptibility is investigated through the calculated S=O index (Arafat et al., 2020). The method of aging and existence of particulates greatly affects the sulfoxide index so that it should not be considered a reliable indicator for determining the aging rate of an asphalt binder or bio-asphalt (Arafat et al., 2020). The C=O index, however, is a reliable indicator of oxidative aging (Hofko et al., 2018).
Figure 37

*FTIR Spectra of Original Samples*

*Note.* The average absorbances of the unaged original samples of BSFLO, HW BO, 70CO and 64CO are shown.

Further testing of BSFLO is needed to prove aging resistance in BSFL bio-asphalt. Determining the rotational viscosity of these samples could provide beneficial information on BSFLO use in asphalt binder. Viscosity is an indicative parameter used for estimating asphalt binder’s workability which is important for mixing and construction (Zhang, You, et al., 2021). Ideally achieving higher viscosities at high temperatures is related to an enhanced high-temperature performance (Wang et al., 2012). However, if viscosity is too high then thermal cracking can occur but, if too low viscosity, then this could damage high-temperature properties (Zhang, You, et al., 2021). From observations when evaluating the BSFL bio-asphalts and asphalt binders after being aged for 96 hours, the BSF samples were still semi-solid and slightly
less viscose than the hardened aged asphalt binder controls, as has also been found in WCO modified asphalt binder which lowered viscosity and softening point (Cao et al., 2019). Overall, bio-based oil modification has been seen to decrease asphalt binder stiffness across all temperature ranges which improves low-temperature performance and fatigue performance while decreasing high-temperature performance grade (Lei et al., 2017). The rotational viscosity testing of BSFLO modified asphalt binders would provide more information on the high-temperature performance.

Parallel to literature where short-term aging using RTFOT showed no significant increase in the carbonyl area while differences between unaged and PAV, or long-term aged samples were significant, the results in this study were similar (Hofko et al., 2018). Even though RTFOT and PAV were not used, Table 4 shows that FTIR could not distinguish significant differences between unaged samples and samples aged for the first aging session of 48 hours at 110°C. However, after 96 hours of aging FTIR could demonstrate significant differences between most samples shown in Figures 29, 30, 31, 33, and 36. Overall, the increase of the carbonyl peak and area is a relative indicator of oxidation while the peak is not an absolute indicator of oxidation (Hofko et al., 2018).

There are indications of high variances in the samples used for this study. Testing for significant differences with more samples would be more ideal and would increase precision. For example, in Figure 14 there is some indication that the 70-5BSF sample could have significantly lower C=O area when compared to the 70CO sample after 96 hours of aging if the variances were lower. More significant differences could be revealed if more samples were used. Another example is in samples 70-10BSF, 64-5BSF, and 64-10BSF which did not show significant differences between unaged and aged samples shown in Figures 32, 34, and 35. The p values
were .06, .06, and .07, which are close to showing significant differences but are not statistically significant or are less than .05. Again, more samples could have determined significant differences between these samples after aging.

**Conclusion**

Overall, FTIR testing is a useful method for assessing functional groups in asphalt binder and bio-based oil modified binders. The IR spectra can distinguish between an asphalt binder and BSFLO modified binder but not between PG 70-22 and PG 64-22 asphalt binders (Figures 6-17). C=O concentrations increase with aging for all samples, except the PG 64-22 samples after 48 hours which showed a reduction in the carbonyl index area but then an increase to a similar area as PG 70-22 after 96 hours which could indicate more samples are needed (Figures 19-22).

Depending on aging duration, the carbonyl index can distinguish between unaged samples and samples aged for 96 hours (Figures 29-36) but, not for 48 hours of aging as shown in Table 3. Since there are significant differences in unaged samples and samples aged for 96 hours (Figures 29, 30, 31, 33, and 36) while there are no significant differences between aged BSFL bio-asphalts and asphalt binders (Figures 23-28) there is potential for the addition of BSFLO to have no negative effects on aging resistance in asphalt performance. Further testing is needed however, as a sustainable input for oil production, BSFL biomass applied in modified asphalt binder production could provide renewable biomass useful in decreasing negative environmental effects of the asphalt industry.
References


# Appendix A

Number of Samples Used

<table>
<thead>
<tr>
<th></th>
<th># Samples</th>
<th>Controls</th>
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## Appendix B

### Sample Descriptions of Wood-Based BO

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<th>Sample</th>
<th>Label</th>
<th>Origin</th>
<th>Description</th>
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<td>Wood-based BO</td>
<td>HW</td>
<td>Living Webb Farms</td>
<td>A black thick solid BO, created from a mixture of pine, oak, poplar, and small amounts of walnut trees</td>
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<tr>
<td>5% HW with 70CO</td>
<td>70-5HW</td>
<td>Lab created</td>
<td>A black, solid mixture of 5% HW BO with PG 70-22 asphalt binder</td>
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<td>10% HW with 70CO</td>
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<td>Lab created</td>
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</table>
Vita

Hyla Marguerita Zouzias was born in Puerto Rico, a territory of the United States of America, to Panagiotis and Rachel Zouzias. She graduated from Hoggard High School in Wilmington, NC, in May 2017. The following fall, she entered Appalachian State University to study Sustainable Technology, and in May 2021 she was awarded Bachelor of Science degree. While finishing the undergraduate degree, Ms. Zouzias was accepted into the accelerated admissions graduate program at the same university, allowing her to take graduate level courses before becoming a full-time graduate student. In the fall of 2021, while working as a graduate assistant, she studied toward a Master of Science in Technology degree with a concentration in Appropriate Technology at Appalachian State University. The M.S. was awarded in December 2022. Ms. Zouzias is an active volunteer in the Watauga County Farmer’s Markets and continues to provide consultations on composting within the community. She resides in Boone, NC.