REVIEW ON RHEOLOGICAL CHARACTERIZATION OF BIO-OILS/BIO-BINDERS AND THEIR APPLICABILITY IN THE FLEXIBLE PAVEMENT INDUSTRY

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ABSTRACT
This paper mainly presents a qualitative review on to what extent the bio-oil has the potential to replace asphalt binder for a sustainable, flexible pavement industry. The current research comprises reviews on the rheological characterization of pure bio-oils and bio-oil modified binders (bio-binders) investigated in the literature. The literature showed that several sources of bio-oils have the potential to contribute to the flexible pavement industry. This research mainly discusses the high-temperature properties, especially viscosity for the construction process (mixing and compaction) and viscoelasticity for the elevated temperature of in-service roads. This review paper encourages orientation towards these kinds of renewable sources of binders in the flexible pavement industry regarding economics, sustainability, and environmental aspects. All reviewed bio-oils in this work, which are waste wood, switchgrass, and waste cooking oil (WCO), could provide a partial or entire substitute binder as they have excellent compatibility with conventional asphalt. Like asphalt, several bio-oils are thermo-plastic viscoelastic and are very susceptible to temperature change. Additionally, they have relatively lower viscosity at mixing and compaction temperatures, which could be reflected by saving energy in the construction process.

Keywords: Bio-Binder, Bio-Oil, DSR, Dynamic Viscosity, Viscoelasticity.


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1. INTRODUCTION

In recent years, the crude oil situation has started to evolve into a crisis [1, 2]. During the 20th century, this crisis did not exist, since crude oil was dominant as the most significant energy and flexible pavement source. Consecutively seeking innovative binders to partially or entirely replace asphalt binders became a new research direction for a sustainable, flexible pavement industry [1, 3, 4]. This research approach deserves investigation due to two significant reasons: (1) crude oil diminishment associated with the sharp increase in asphalt price, and (2) crude oil as a nonrenewable source of a flexible paving binder [5, 6]. It is expected that the world will confront no crude oil by the middle of the 21st century [3, 7]. In order to solve this crisis, many researchers have investigated different sources of bio-oils [8]. However, this kind of research still needs more investigation to chemically and rheologically assess the applicability of bio-oil as a partial or entire asphalt replacer. The literature showed three categories of asphalt replacement by bio-oil: (1) 100% asphalt replacer (i.e., zero percent asphalt), (2) asphalt modifier (up to 10% replacement), and (3) asphalt extender [9]. For instance, Yang et al. (2014) reported a replacement of 5-10% of asphalt by bio-oil would not affect the results of the pavement performance tests [10]. Peralta et al. (2014) worked on a replacement of 20% of asphalt by bio-oil/bio-binder; justifying partial replacement of asphalt (20%) could achieve a relatively greater economic advantage in the paving industry [11]. Additionally, researchers made attempts to replace the asphalt entirely by bio-binder [8].

Literature showed that the bio-oil produced from biomass (e.g., oakwood, switchgrass, and cornstover) or bio-waste (e.g., waste cooking oil (WCO)) products for a partial or entire replacement to asphalt were investigated by several researchers [12]. The simplest and most widely used method to extract bio-oil from biomass is the fast pyrolysis method [9, 13]. The concentration of bio-oil in the biomass depends on the feedstock material. For instance, oakwood contains about 69% bio-oil, while cornstover and corn fiber contain about 37% and 56%, respectively [14]. Raouf (2010) stated that bio-oil could be defined as a dark-brown liquid produced from the rapid heating biomass in vacuum conditions [15]. Sun et al. 2016 [16] reported that WCO is mainly composed of saturates, aromatics, resins, and asphaltene (SARA fractions, the same main composition of asphalt) [16]. That is why the compatibility between these kinds of innovative bio-binders with asphalt exists, and we encourage following this trend of research in the massive, flexible pavement industry. However, the literature showed that asphaltene in bio-oil is relatively in a lower concentration compared to conventional asphalt [16]. Additionally, bio-oil potentially may contain relatively more saturate and resin concentrations [16].

Bio-oils extracted from waste wood (e.g., cornstover, oakwood, and switchgrass) have the potential to be utilized as flexible paving binders, since some of them contain a high amount of lignin (about 82% [14]) and low water content (about 16%) [14], [15]. Researchers used bio-oils in binder production in different scenarios: original (no treatment), dewatered, and/or modified (e.g., polymer) [10, 17]. However, because of the high volatiles of cornstover, oakwood, and switchgrass bio-oils, Raouf (2010) recommended no heat treatment of these kinds of bio-oils beyond 120°C since their properties may change beyond this temperature [15]. One of the dewatered (pretreated) bio-oil methods used in research by Peralta et al. (2014) was as follows: water was removed utilizing Silverstone Shear Mill under the conditions of 3000 rpm and 110°C, starting from 90°C with increments reaching 110°C. This last temperature was applied up to the boiling stop, indicating little-to-no moisture after about 60 min [11].

In the current research, the authors aimed to focus on the rheological characterization of different kinds of bio-oils that have already been investigated in the literature (e.g., waste
wood, switchgrass, and WCO). The significant distinction of this work was how to create an innovative renewable binder that could partially or entirely replace the asphalt binder. This replacement could be beneficial in terms of sustainability, economics, and environmental concerns that are related to the flexible pavement industry.

2. REVIEW ON METHODS USED IN BIO-OIL/BIO-BINDER CHARACTERIZATION

2.1. Dynamic Viscometer

Viscosity could be defined as the physical material characteristic that describes the resistance of liquids to flow [18]. It is essential to show the workability of the binder during the construction process (mixing and compaction). Therefore, it is an initial characterization of binder to decide whether it could be accepted or not [15]. Likewise, it is a property that could determine if the binder is Newtonian or non-Newtonian by measuring the shear stress (or viscosity) via a wide range of shear rates. Asphalt binders and asphalt-like materials most likely behave as Newtonian fluids (stress response does not depend on shear rate) at required testing temperatures, which are above 100°C [19]. The rotational viscometer is the most commonly used device for measuring the binder viscosity, according to ASTM D4402 [20]. Equation 1 depicts how to determine the viscosity of the binder at construction temperatures.

\[
\nu = \frac{\tau}{\dot{\gamma}}
\]

where
- \(\nu\) Dynamic viscosity in Pa.s
- \(\tau\) Shear stress in Pa
- \(\dot{\gamma}\) Shear strain rate in s\(^{-1}\)

2.2. Viscoelasticity at Elevated In-Service Temperatures

In the Superpave grading system, viscoelasticity for conventional asphalt binder at elevated temperatures is assessed by G*/Sin\(\delta\), in which G* represents the complex shear modulus, and \(\delta\) represents the shift angle. The complex shear modulus is defined as peak shear stress divided by peak shear strain [4]. It is also defined as the total resistance of the binder when repeatedly sheared [19]. It is only a property while the material is viscoelastic, which has the two properties at the same time (i.e., elastic property and viscous property), and each one has its modulus: elastic (storage) modulus (G') and viscous (loss) modulus (G'\(_\nu\)). Consecutively, G* is a function of G' and G'\(_\nu\). On the other hand, the phase angle (shift) is the ratio of the elastic and viscous components [4]. The G*/Sin\(\delta\) denotes the rutting parameter, which is a rheological parameter that evaluates the ability of the flexible paving binder to resist rutting, which is one of the major distresses that impacts flexible pavement. The higher the G*/Sin\(\delta\) value, the higher the shearing (rutting) resistance during sustained loads and high temperatures [8]. In other words, the higher G*/Sin\(\delta\) corresponds to a stiffer (higher G*) and more elastic (lower \(\delta\)) material. The Superpave grading system requires G*/Sin\(\delta\) to be greater than 1.0 kPa for the original (unaged) binder at a high-temperature grade, which is required for quality assessment [21]. However, the same parameter is required to be 2.2 kPa for the short-term aging process (construction process) [21], which is stimulated by the rolling thin film oven (RTFO) in the laboratory [22].

The dynamic shear rheometer (DSR) is the most commonly used device to measure the rheological properties of binders used in the flexible pavement industry. It can evaluate the high-temperature rutting resistance and the intermediate temperature grade, which correspond to the fatigue cracking resistance [19]. The DSR has a variety of approaches used to evaluate
specific distress. The scope here is evaluating the bio-oil influence as the binder or co-binder regarding the high-temperature grade, which corresponds to the rutting resistance, particularly on hot summer days. As mentioned above, the Superpave grading system requires G*/Sinδ in order to measure the binder rutting resistance. However, other researchers see that nonrecoverable creep compliance (Jnr) simulates the field rutting in a better manner, specifically for modified binders [12, 23]. The idea of this test is to shear the binder for 1 sec and rest for 9 sec under the DSR plates using 25-mm parallel plates with a gap of 1 mm [24]. Likewise, the master curve is an excellent tool to shift the rheological property curve (e.g., G’, G”, G*, δ, or G*/sinδ) to any reference temperature [4], and the corresponding frequency range could go beyond the rheometer capabilities. This shift is applied by the time-temperature superposition principle.

3. VISCOSITY EVALUATION OF BIO-OILS/BIO-BINDERS

3.1. Waste Wood

Peralta et al. (2014) studied the viscosity of bio-oil (extracted from fast pyrolysis of oakwood on the rotational viscometer) as a function of time at 95°C [11]. The results showed a wide range of viscosity change with time, which was from 0.0425–0.2075 Pa.s via 8.5 hours in an exponential function (ν = 0.037629e0.0032t, in which ν in Pa.s and t (time) in minute) while the rotational speed was constant (20 rpm) [11]. The authors justified that by the polymerization due to phenols combined with furfural & volatilization of some free water [11, 14]. This exponential function reflects the susceptibility of bio-oil viscosity to the time evolution, as shown in Figure 1.

![Figure 1](http://www.iaeme.com/IJCIET/index.asp)

Figure 1 Change in oakwood bio-oil viscosity with time at 95°C [11]

Peralta et al. (2013) investigated a 100% bio-binder extracted from red oakwood with using tire rubber as a modifier, creating modified bio-oil (MBO) [25]. Tire rubber represents non-colloidal suspended particles in the rubber-modified bio-oil. The authors investigated the influence of increasing the concentration of tire rubber on the dynamic viscosity, as shown in Figure 2. Two sources of rubbers were used: cryogenic (cryo) and ambient (amb). Peralta et al. (2014) saw that rubber particles in any rubber-modified binder provide higher mixing and compaction temperature than expected, justifying that by the effect of rubber particles that might present a fake (higher) binder viscosity [11]. The viscosity investigation was applied in two conditions: (1) whole matrix (cryoMBO and ambMBO) and (2) Residue after extracting the suspended rubber particles, Res(cryoMBO) and Res(ambMBO) [25].
The rubber percent and viscosity relationship seems linear. The rubber interacted with the bio-oil and released some components as it could be shown by increasing the viscosity of the residue (after extracting rubber particles), as shown in Figure 2. Furthermore, one could observe that the cryogenic rubber component release had a much higher impact on the viscosity increase compared to the ambient rubber. However, the viscosity increase of ambMBO was more evident than cryoMBO on the matrix scale. From the suspension rheology viewpoint, the matrix viscosity increase could be justified by raising the suspended particle concentration. Peralta et al. (2013) reported that the rubber particle indicated a higher viscosity [25]. Additionally, the rubber particles were supposed to be considered additional aggregate in the overall mix [11]. The authors also compared the viscosity of bio-oil to conventional asphalt as a function of temperature. The oakwood bio-oil had the potential to achieve a comparable viscosity to conventional asphalt (in this case, 50/70 and 160/220 according to the penetration grading system), but at much lower temperatures. Figure 3 shows approximate viscosity trends showing to what extent the bio-oil could yield a similar viscosity trend to conventional asphalt, but at lower temperatures [25]. This indicates lower energy required for mixing and compaction, which is desirable in the construction process [25].

Figure 3: Comparison between viscosities as a function of temperature for bio-oil vs. conventional asphalt [25]

3.2. Switchgrass

Raouf and Williams (2009) reported that switchgrass could not be used without pretreatment as a 100% asphalt replacer because of including water and volatile materials [26]. In 2010, they investigated pretreated switchgrass rheological properties according to temperature and shear dependence [9]. The benefit here was to show to what extent this kind of bio-oil was close to conventional asphalt. In their work, authors compared two conventional asphalts (AAM and AAD) to bio-oil and polymer-modified bio-oils (Bio-binders) (in which three
different polymers were added to bio-oil in two concentrations (2% and 4%) creating six different blends).

The study showed that viscosity measurements resulted in similar exponential trends for all blends; viscosity significantly decreased while the temperature increased, with almost identical trends beyond 100°C for all bio-binders. However, bio-oils or bio-binders resulted in relatively lower viscosities compared to conventional asphalt. This point is distinctive regarding the construction process (i.e., lowering the required temperature for mixing and compaction, hence lowering the required energy/cost), which agrees with [25]. On the other hand, measuring the viscosity of bio-binders as a function of shear strain rate resulted in shear-thinning from zero shear viscosity to about 20 rpm; hence, it resulted in constant viscosity higher than 20 rpm. Shear-thinning is desirable regarding testing rheometers and the construction process (i.e., better workability). Furthermore, 20 rpm rotational speed is recommended for asphalt binders while using the rotational viscometer (RV) at elevated temperatures used in the construction process, according to AASHTO T316 [23]. Little-to-no effect of increasing shear rate on the conventional asphalt binders was also noticed. Overall, most of conventional asphalts behave Newtonian at high (construction) temperatures (beyond 100°C). In other words, there is no change in viscosity with shear rate evolution. Additionally, not all bio-oil blends yielded the same shear-thinning behavior. The authors in that work saw that shear-thinning behavior was a function of polymer type and concentration in the bio-binder [9].

3.3. Waste Cooking Oil (WCO)

Most of research implemented on WCO in asphalt industry was on how to utilize it as a natural asphalt rejuvenating agent for aged asphalt and very stiff virgin asphalt [16, 27]. In general, the asphalt rejuvenating agents are used to revive aging and brittle asphalt pavements [28]. Since asphalt loses some of its aromatics during its aging and oxidation, rejuvenators could play a significant role in compromising this brittle asphalt with aromatics, which could partially or entirely retrieve its chemical, physical, and rheological characteristics.

Sun et al. (2016) investigated WCO as a modifier to conventional asphalt in concentrations of 2, 4, 6, and 8%. During this study, viscosity decreased while increasing WCO in the blend because of the dilution effect, which makes it compatible with the above-mentioned bio-oils [16]. Additionally, Zargar et al. (2012) investigated the effect of using the WCO as a rejuvenating agent to aged binders in a concentration of 1–5% [27]. The authors reported that 3–4% of WCO could rejuvenate an aged binder 40/50 (pen-grade) to be comparable to 80/100 with respect to physical and rheological characteristics.

Fast pyrolysis bio-oils (e.g., oakwood, switchgrass, and cornstover) have different characteristics compared to WCO. Fast pyrolysis bio-oils have the potential to be asphalt replacers to a great extent, as they are asphalt-like materials (viscoelastic, temperature-susceptible, comparable viscosity, etc.); however, WCO is a pure liquid at room temperature, which could be added to asphalt binder in very limited concentrations.

3.4. Summary of Bio-Oil/Bio-Binder Viscosity

It was clear that bio-oil, in general, had the potential to provide a partial or entire replacement to conventional asphalt (petroleum-based binder) in terms of viscosity investigation regardless of the source of bio-oil. All investigated fast-pyrolysis bio-oils provided a similar tendency to petroleum-based binders. However, they could provide comparable viscosities at relatively lower temperatures, which is desirable in the construction (mixing and compaction) process for lower energy consumed, hence lower construction expenses. On the other hand, WCO
provided much lower viscosity, which is a pure liquid at room temperature. For instance, WCO viscosity was measured by Sun et al. (2014), and it resulted in 146.3 cP at room temperature [16].

4. VISCOELASTICITY OF BIO-OILS/BIO-BINDERS AT ELEVATED TEMPERATURES

4.1. Waste Wood

Peralta et al. (2012) investigated the rheological properties of bio-oil as bio-binder (i.e., 100% asphalt replacer) produced from the fast pyrolysis of oakwood. The critical (pass/fail) temperature was investigated to evaluate the rutting resistance of four kinds of bio-binders containing bio-oil with either cryogenic (cryo) tire rubber, or ambient (amb) tire rubber. These four bio-binders were coded A, B, D, and E (“A” and “D” contain 90% bio-oil and 10% cryo and amb, respectively, and “B” and “E” contain 85% bio-oil and 15% cryo and amb, respectively) [8]. Figure 4 shows the critical temperature of conventional asphalt PG64-16 and the above-mentioned four bio-binders. They were investigated original (before heat treatment), heat-treated, and bio-binder residue (bio-binder residue after extracting tire rubber).

The untreated bio-oil had a grade of 47.87°C, and the heat-treated bio-oil had a slightly higher grade (49.20°C). However, the tire rubber significantly enhanced its grade. This enhancement indicated a better rutting resistance performance, which was attributed to an overall improvement in the net elastic and stiffness properties. However, 15% of rubber yielded a potential of PG64, while 10% of rubber yielded a potential of PG58.

![Figure 4](https://via.placeholder.com/150)

Figure 4 Pass/fail elevated temperature of conventional asphalt (PG64-16) vs. different bio-binders [8]

Likewise, Peralta et al. (2013) evaluated the viscoelasticity of cryogenic-rubber modified bio-oil (cryMBO) and compared it with conventional asphalt (PG64-22) and (PG64-22 & 20%cryoMBO) by G*/Sinδ master curves at a 20°C reference temperature [29]. The authors show that the G*/SinØ master curve as a function of frequency was similar when comparing PG64-22 with cryoMBO or even PG64-22 & cryoMBO. This may indicate that rubber could enhance the viscoelasticity of bio-oil, making it comparable to conventional asphalt.

In a paper by Gao et al. (2018), the authors investigated the viscoelastic property of a bio-oil SBS (styrene-butadiene-styrene) modified binder. The bio-oil used in that work was produced from the waste wood (sawdust). The SBS was utilized as an enhancer mainly to compensate for the loss in stiffness that occurred by the bio-oil. The control binder was represented by adding 1% SBS to the conventional binder. The bio-oil was added to the SBS-
modified asphalt in four concentrations: 5%, 10%, 15%, and 20% by wt. of SBS-modified asphalt (mentioned here as 5% bio-binder, 10% bio-binder, 15% bio-binder, and 20% bio-binder). The G*/sinδ master curves were utilized to judge the contribution of sawdust bio-oil to the SBS-modified asphalt. These master curves were created according to multiple temperatures and frequencies.

The authors showed that the similarity in trends among the four bio-binders, the conventional asphalt, and the SBS-modified asphalt (control binder) from low frequency to high frequency. The G*/sinδ value increased with increasing frequency. The 5% bio-binder and 15% bio-binder yielded relatively lower trends compared to the 10% bio-binder and 20% bio-binder, but the 10% bio-binder and 20% bio-binder were almost identical to the SBS-modified asphalt and the conventional asphalt. This indicated that the 10% bio-binder and 20% bio-binder had a better rutting resistance via a wide range of traffic speeds (frequencies) and temperatures. Overall, the study indicated the potential associated with the sawdust bio-oil to provide a performance equivalent (or higher) to the conventional asphalt in the attendance of an enhancer such as SBS.

Both studies by Peralta et al. (2013) and Gao et al. (2018) were compatible regarding a similar tendency of G*/Sinδ master curves when comparing the bio-binders with conventional asphalt.

4.2. Waste Cooking Oil (WCO)

Wen et al. (2012) investigated bio-oil established from WCO. Authors reported that WCO could be polymerized to produce bio-asphalt by adding it to conventional asphalt, creating an innovative binder [12]. The study showed that the WCO had a tent to decrease the stiffness of the conventional asphalt. However, WCO improved the low temperature cracking performance tested by the bending beam rheometer (BBR). Overall, the study claimed that bio-asphalt increased the non-recoverable compliance (Jnr) of conventional asphalt, indicating higher susceptibility to rutting compared to the pure conventional asphalt. Likewise, the authors emphasized that this conclusion also complied with the G*/Sinδ (rutting parameter) evaluation, accepted by the Superpave grading system [18].

In the study, mentioned above, by Sun et al. (2016), the bio-binders presented similar trends like conventional asphalt; however, the master curves showed their horizontal shift to the right (either for complex modulus or phase angle) with increasing the WCO concentration [16]. This shift indicated that the addition of WCO bio-oil lowered the complex modulus (G*) and increased the phase angle (δ).

4.3. Summary of Bio-Oil/Bio-Binder Viscoelasticity

It was clear that WCO bio-oil might not be sufficient as a comparable binder to the petroleum-based binder, even with polymerization. It seemed to have high liquidity that could not help for increasing the overall binder stiffness and elasticity at high in-service pavement temperature. However, Wen et al. (2012) claimed that it could enhance the low-temperature cracking (thermal cracking resistance) [12]. Nevertheless, this point is out of the scope of the current review.

5. APPLICABILITY OF BIO-OILS IN PAVING INDUSTRY

We may divide the bio-oils into two categories regarding asphalt replacement. Some of them behave as rejuvenating agents such as WCO, and others behave as replacers to asphalt binders such as oakwood. Generally, the rejuvenating agents have liquid-like behavior (i.e., more viscous and less elastic). These rejuvenating agents refresh the binder (either virgin or
recycled) with more aromatics, which is desirable during binder aging/oxidation via time or very stiff virgin binder that we aim to decrease its stiffness while increasing its softness at very low temperatures resisting thermal cracking. In other words, these aromatics decrease the binder matrix stiffness to an acceptable limit, but also they increase the resistance to low-temperature cracking (thermal cracking). On the other hand, bio-oils as asphalt replacers have similar properties to conventional asphalt, particularly when enhanced by modifiers such as crumb rubber [30]. Overall, these kinds of bio-oils are thermo-plastic viscoelastic, which are susceptible to temperature change [11]. In that case, this kind of bio-oil has a competitive intent to be a 100% asphalt replacer, such as research done by Peralta et al. [8]. Even though most of the investigated bio-oils resulted in a relatively lower stiffness compared to conventional asphalt, it could be modified by enhancers such as tire rubber, polymers (e.g., SBS), etc. to balance a performance required by a comparable conventional asphalt. On the other hand, bio-oil presented a prospective behavior at low temperatures indicating an excellent resistance to thermal cracking. As an example, Peralta et al. (2012) concluded a 100% bio-oil binder (bio-binder) with a Superpave grade of up to PG64-22 [8], which is comparable to most of the locations in the United States.

6. CONCLUSIONS
Overall, this review showed that bio-oils had the potential to be utilized in asphalt replacement in three divisions: (1) 100% asphalt replacer (i.e., zero percent asphalt cement), (2) asphalt modifier (up to 10% replacement), and (3) asphalt extender, according to the bio-oil nature and its modification. Bio-oils also could be divided into two categories: rejuvenators and replacers. Rejuvenators could refresh the binder, either virgin or recycled (reclaimed asphalt pavement (RAP) and reclaimed asphalt shingles (RAS)), with more aromatics. These aromatics are desirable after binder aging/oxidation with time. In the case of a very stiff virgin binder, we aim to decrease its stiffness while increasing its softness at very low temperatures in order to resist thermal cracking. For instance, WCO did not provide a comparable binder, even after polymerization. It tended to have more liquidity (less stiffness and elasticity, evaluated by lower G* and higher δ, respectively). On the other hand, some kinds of bio-oils, such as waste wood, could provide a 100% replacer to conventional asphalt. However, it could need an enhancer such as a polymer (e.g., SBS) or tire rubber to compensate for the viscoelastic performance required by a corresponding conventional asphalt (higher stiffness and elasticity, evaluated by higher G* and lower δ, respectively).

It was clear that bio-oil, in general, had the potential to provide a partial or entire replacement to conventional asphalt (petroleum-based binder) in terms of viscosity investigation, regardless of the source of bio-oil. All investigated bio-oils provided a similar tendency to petroleum-based binders. However, they could provide comparable viscosities at relatively lower temperatures, which is desirable in the construction (mixing and compaction) process for lower energy consumed, hence lower construction expenses.

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REFERENCES


