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An overview of utilization of bio-oil in hot mix asphalt

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Abstract: Due to the high prices of crude oil, the price of asphalt binder has increased tremendously. Thus, many researchers have attempted to find acceptable viscosity cheaper asphalt for pavement construction. The asphalt industry is constantly attempting to reduce its emissions as concerns are growing on global warming. This is done by decreasing the mixing and compaction temperatures of asphalt mixtures without affecting the properties of the mix which is possible through numerous available technologies in the industry. One of these techniques is by using bio-oil technology as a modifier or an extender of the base asphalt binder in pavement mixtures. This paper is an attempt to give general picture of current state of practice for bio-oil presenting the benefits of using of bio-oil technique, producing of bio-oil, and physical and chemical properties of bio-oil. Additionally, the performance of bio-oil modified bitumen is described here as well as the mechanical properties of bio-oil mixtures.

Key words: *Bio-oil Production; Bio-oil technique; Bio-asphalt properties; Bio-oil performance*

1. Introduction

The increasing demand for petroleum derived products coupled with decreasing world crude reserves has led to substantial increases in asphalt pricing. The dynamics of world resource economics suggest that all industries, including the asphalt pavement industry, should be exploring economically, socially, and environmentally sustainable approaches to development. Increased environmental regulations and the rising costs of asphalt binder have encouraged researchers to investigate alternative binders that can be used for hot mix asphalt (HMA). Though, on a limited scale, a number of noteworthy research works are being conducted worldwide on producing bio-binders from biological resources such as vegetation and forest waste, yard waste, and sugar cane molasses (Mills-Beale et al.; 2014). This study focused on literature using bio-asphalt as a possible alternative binder to petroleum based asphalt.

2. Benefits of using bio-asphalt:

Bio-asphalt is produced by upgrading bio-oils produced from the rapid heating of biomass in a vacuum condition. Bio-oils can be described as dark brown, free-flowing organic liquids that are comprised mainly of highly oxygenated compounds. In other words, it is the liquid produced from the rapid heating of biomass in a vacuum condition (Peralta et al., 2012).

Bio-asphalt have many advantages over fossil asphalt as they are renewable, environmentally friendly, provide energy security, and present a great economic opportunity for the United States. However, until now, almost no research has studied the applicability of utilizing bio-oils as a partial or full replacement alternative of bitumen in the pavement industry. The limited number of references produced on this matter show that this goal may be achieved very soon by the application of a new technology with the aid of polymer addition (Peralta et al., 2012).

Although research into the development and application of bio-binders as a useful sustainable component in asphalt paving is relatively new in the field, a number of research activities are noteworthy in this area. Researchers are beginning to focus on bio-binders as a sustainable substitute to crude asphalt and build on earlier developments in the mid-1950s (Mills-Beale et al. 2014).

Vignesh et al., (2013) have summarized the benefits of using bio-asphalt as an alternative for the crude oil based asphalt as following:

1- Produced from domestic non-food resources.
2- Decreases the demand for imported petroleum.
3- Can be a direct replacement for petroleum based liquid asphalt as an additive, modifier or extender.
4- Reduces carbon footprint.
5- Can lower the production temperature of hot mix asphalt, which may decrease paving costs by 20%.
6- Reduces greenhouse gas emissions up to 30% because less energy input is required.
7- Provide an anti-oxidant effect which could increase the service life of pavements.
8- Can extend the grade range of asphalt.
9- Can be priced competitively below today's asphalt prices without subsidies.

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3. Background of biomass used in producing bio-oil

Biomass is anything living matter on earth in which solar energy is stored. By the process of photosynthesis, plants produce biomass continuously (Demirbas and Balat 2006). According to Goyal *et al.* (2006), biomass resources can be divided into two broad categories, e.g. natural and derived materials and then subdivided into three categories that can be listed as follows: (1) wastes that include but are not limited to agricultural production wastes, agricultural processing wastes, crop residues, mill wood wastes, urban wood-wastes, and urban organic wastes, (2) forest products that include but are not limited to wood, logging residues, trees, shrubs and wood residues, sawdust, bark, and (3) energy crops that include but are not limited to short rotation woody crops, herbaceous woody crops, grasses, starch crops, sugar crops, and oilseed crops.

Bio-oils derived from wood have specific oxygenated compounds that are present in relatively large amounts. A large fraction of the bio-oils is the phenolic fraction which consists of relatively small amounts of phenol, eugenol, cresols and xylenols and much larger quantities of alkylated (poly-) phenols (water insoluble pyrolytic lignin). This phenolic fraction has showed good performance as an adhesive for waterproof plywood as stated by Demirbas and Balat (2006).

As a result of the high oxygen content, the energy content of the bio-oils is about half of that crude oil. It is also plagued by poor volatility, high viscosity, and corrosiveness. Raw bio-oil can contain between 10 and 30% by weight of water and hundreds of various oxygenated organic compounds. Some of these components are highly reactive and can cause pyrolysis oil to be unstable, resulting in higher water content and an increase in viscosity over time as declared by Mullen *et al.* (2008).

3.1. Production of bio-oils by pyrolysis:

Pyrolysis is performed in the absence of oxygen. This process converts the organic materials in the feedstock to a complex mixture of oxygenated compounds. Three separate products are produced during pyrolysis: a condensable liquid (pyrolysis oil), a charcoal coproduct, and a mixture of noncondensable gases (syngas). Pyrolysis oil is the target product of the fast pyrolysis process with an approximate density of 10 lb/gal at 59°F (1.20 kg/liter at 15°C) with higher heating value (HHV) energy content of approximately 18 MJ/kg. In fast pyrolysis, the feedstock is rapidly heated to bring the feedstock particles to temperatures of 752°F to 1,022°F (400°C to 550°C) in less than 2 seconds. A thin particle dimension facilitates rapid heat transfer and improves pyrolysis oil yield and quality (Steele et al., 2012).

Since the oil crisis in the mid-1970s, considerable effort has been directed toward the development of processes for producing liquid fuels from biomass. According to Oasmaa *et al.* (1999), one of the most efficient methods for such conversion is pyrolysis. Historically, pyrolysis was used during the ancient Egyptians times as tar was produced for caulking boats and certain embalming agents (Mohan *et al.* 2006). Through pyrolysis of different sources of biomass, a wide range of fuels, solvents, chemicals, and other products can be produced (Demirbas 2008). There are different methods to convert different sources of biomass into bio-fuels or hydrogen as reported by Demirbas and Balat (2006). Table 1 shows the merits and demerits of each method. In pyrolysis, pyrolysis liquid, char and gas are the main products as shown in Fig. 1 (Peralta et al., 2012).

Table 1: Merits and Demerits of Different Types of Pyrolysis (After Raouf and Williams 2010)

Conversion process	Merits	Demerit
Steam gasification	Maximum product can be obtained	Significant gas conditioning is required
Fast pyrolysis	Bio-oil and chemicals are produced	Changes of catalyst deactivation
Solar gasification	High hydrogen yield can be obtained	Requires effective collectors
Supercritical fluid extraction	Products can be obtained without gasification	Selection of supercritical medium
Microbial fermentation	Wastewater can also be treated simultaneously	Selection of suitable microorganisms

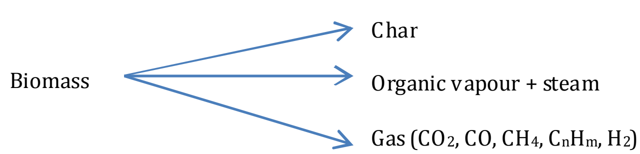

Fig. 1: The main products of pyrolysis (After Lindfors, 2011)

Generally, fast pyrolysis does not generate any waste because the bio-oil and solid char can each be used as a fuel and the gas can be recycled back into the process (Mohan *et al.* 2006). According to Goyal *et al.* (2006), the bio-oils obtained from pyrolysis methods have many industrial uses that include but are not limited to use, as a combustion fuel, a transportation fuel to substitute fossil fuels, a liquid smoke, a preservative, a raw material to produce chemicals and resins, a binder for palletizing and briquetting of combustible organic waste materials, or an adhesive material. Furthermore, pyrolysis gases which have significant amount of carbon dioxide along with methane can be used as a fuel for industrial combustion purposes.

Fast pyrolysis has four main processes that can be summarized as follows: (1) very high heating and heat transfer rates, (2) a carefully controlled pyrolysis reaction temperature (in the range of 425-500°C), (3) short vapor residence times (typically < 2s), and (4) rapid cooling of pyrolysis vapors and aerosols to produce bio-oils (Mohan *et al.,* 2006).

The bio-oil as, shown in Fig. 2 below, is a liquid fuel containing lignin that can be combusted by some engines or turbines for the electricity generation purpose. Since the bio-oil can have lignin contents of more than 35% by weight, using bio-oil as an antioxidant in asphalt production could prove to be an economical alternative to conventional methods while being conscious of the environment and increasing the longevity and performance of asphalt pavements (Tang, 2010).

Fig. 2: Bio-oil Sample (After Tang, 2010)

The yield of the liquid product is very dependent on the temperature, heating rate and residence time of the raw material. The highest liquid yield is obtained with fast or flash pyrolysis, where the biomass is heated up very fast (1000 ℃/s) to a moderate temperature (500 °C) during very short vapour residence time (<2 s). In this case the organic liquid yield can be up to 65 wt- % for sawdust (Lindfors, 2011).

Generally, fast pyrolysis is used to obtain high-grade bio-oil. Organic biomass consists of biopolymers, such as cellulose, hemicelluloses, and lignin. Because of the different sources of biomass, the amount of production of the liquid bio-oils, solid char, and noncondensable gases varies. For example, fast pyrolysis processes produce about 60 to 75 wt% of liquid bio-oil, 15 to 25 wt% of solid char, and 10 to 20 wt% of noncondensable gases (Mohan *et al.,* 2006).

Fig. 3 shows the 25 kWt fast pyrolysis system developed at Iowa State University by the Center for Sustainable Environmental Technology where bio-oils are produced from different biomass materials (Peralta et al., 2012).

With the bioasphalt plant used for one project, if the facility has available 400 tonnes waste wood/day as feed stock, it will be capable of producing an estimated 8.0 tons of bio-asphalt (Fan *et al.,* 2011).

4. Elemental analysis of bio-asphalt fractions:

The chemical composition, and hence the physical properties, of bio-oils depends on the feedstock, pyrolysis condition, and product collection methods. The chemical composition of bio-oils is a crucial factor as it gives insights into quality and stability issues as emphasized by Mullen *et al.* 2008. Bio-oils have five different compounds that can be summarized as follows: (1) hydroxyaldehydes, (2) hydroxyketones, (3) sugars and dehydrosugars, (4) carboxylic acids, and (5) phenolic compounds. Based on the analysis conducted by many researchers, Table (2) displays the chemical composition of the different bio-oils. In addition, the elemental analysis of the bio-oils is a significant factor to be studied to properly determine and predict the characteristics of bio-oils. Table (3) lists the elemental analysis of the different bio-oils based on the available data on the literature review (Mullen *et al.,* 2008).

The three major structural chemical components of biomass which have high molar masses are carbohydrate polymers and oligomers (65%-75%) and lignin (18%-35%). These chemical components consist of cellulose (which is called polymer glucosan), hemicelluloses (which are also called polyose), lignin, organic extractives, and inorganic minerals, as shown in Fig. 4. The weight percent of cellulose, hemicelluloses, and lignin products varies depending on the biomass (Mohan *et al.,* 2006). Generally, in biomass, cellulose is the largest fraction followed by hemi-cellulose, lignin, ash, etc. as stated by Goyal *et al.,* (2006).

Table 2: Chemical Composition of Bio-oils*

Wt (%)	Cornstover	Oakwood/Oak Flour	Switch grass
Cellulose	40	40	41
Hemicellulose	30	26	36
Lignin	14	16	20

* Adopted from Mohan et al. 2008 and Mullen et al., 2008

Table 3: Elemental Analysis of Bio-oils*

Wt(%)	Cornstover	Oakwood/Oak Flour	Switch grass
C	46.50	60.50	47.47
H	5.90	6.50	6.96
O	46.20	34.60	45.19

* Adopted from Mohan et al. 2008 and Mullen et al., 2008

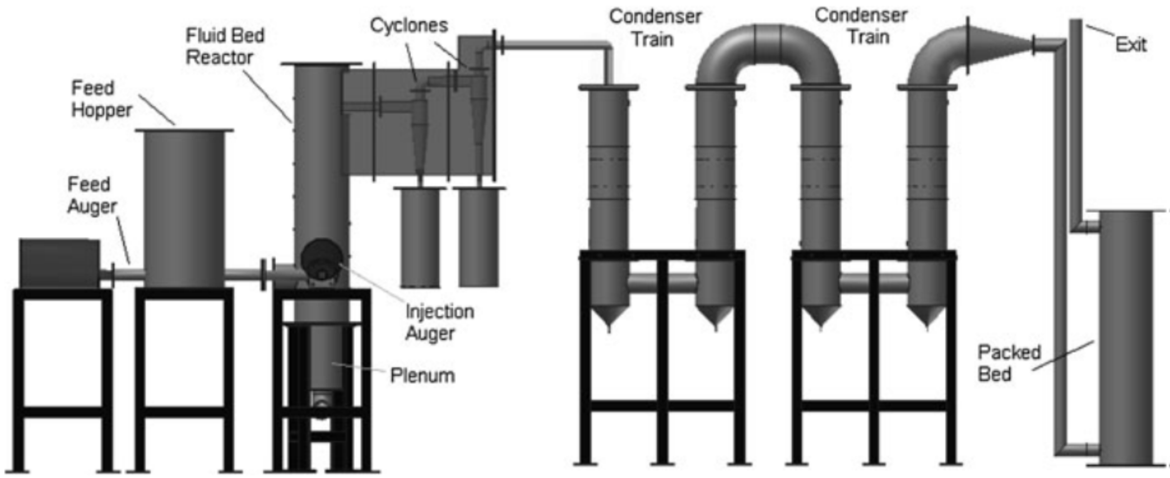

Fig. 3: Schematic of the Bio-oil mass pyrolysis pilot plant (Source: Iowa State University, 2010)

The Carbon (C), Hydrogen (H) and Nitrogen (N) elemental investigations on the bio-asphalt fractions was conducted. In general, the carbon is the highest element followed by the hydrogen and then finally the nitrogen element. Since bio-asphalt from combined wood type sources as an innovative alternative to petroleum-based asphalt binders, a comparative analysis was conducted between this bio-asphalt and one from petroleum and swine waste sources. This comparison is provided in Table (4) from which it is evident that this bio-asphalt from wood chips, sawdust and shavings has the least amounts of carbon, hydrogen and nitrogen elements. The relative amounts of carbon, hydrogen and nitrogen in petroleum-based asphalt has been known to affect the functional or polar group formations and it hypothesized that the same will apply to this wood-waste bio-asphalt (Roberts, 1996). It is believed that this elemental difference will affect the chemical bonding behavior, morphological, rheological and bio-asphalt-modified pavement mixture properties (You et al., 2012).

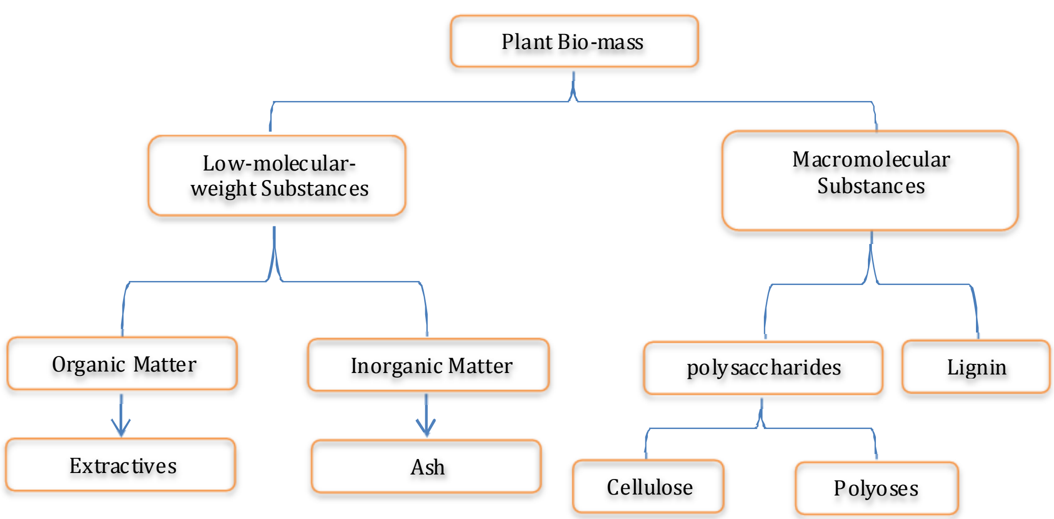

Fig. 4: Chemical Structure of Bio-oils. (Adopted from Mohan *et al*, 2006)

The typical properties of bio-oils generated from wood resources (Mohan *et al.*, 2006) are shown in Table (5) Previous studies showed that bio-oils generated from this process have similar rheological properties as the petroleum asphalt binder (Fini et al., 2010).

Table 4: Elemental composition of asphalt from different sources (after You et al., 2012)

Asphalt type	Carbon %	Hydrogen %	Nitrogen %
Petroleum asphalt (Fini et al. 2011)	81.600	11.600	.800
Swine-waste bio-asphalt (Fini et al. 2011)	71.600	9.800	4.500
Wood-waste bioasphalt	58.800	6.620	0.270
Comparative analysis	Wood-waste bio-asphalt has least amount of all 3 elements		

Table 5: Typical Properties of Bio-oils Generated from Wood Resources (after Mohan *et al.*, 2006)

Physical Property	Value
Moistute Content (wt %)	15-30
Specific Gravity	1.2
Elemental composition (C, H, O, N) (wt%)	(54-58, 5.5-7.0, 35-40, 0-0.2)
PH	2.5
Viscosity at 500°C (cP)	40-100
Distillation residue (wt %)	Up to 50

5. Physical/rheological properties of bio-oils

Due to the complexity of the chemical structure of bio-oils as aforementioned, it is extremely difficult to use chemical analyses to characterize performance. Thus, physical property measurements can be considered as the primary means of studying the applicability and the reliability of the utilization of bio-oils as bio-binders (Raouf and Williams, 2010).

As reported by Garcia-Perez *et al.* (2008), the physical state of bio-oils can be described as follows: "The multiphase complex structure of bio-oils can be attributed to the presence of char particles, waxy materials, aqueous droplets with different natures, and micelles formed of heavy compounds in a matrix of hollocellulose-derived compounds and water." In addition, bio-oils comprise aldehydes, ketones, and other compounds that may react via condensations to form larger molecules during storage, handling, or transportation (Mohan *et al.* 2006). Therefore, these reactions lead to the undesirable changes in physical properties. For example, viscosity and water content can increase, whereas the volatility will decrease (Mohan *et al.* 2006).

The physical characteristics of bio-oils can be summarized as follows: (1) the density of the bio-oil is about 1200 kg/m3 which is higher than the original biomass, (2) the viscosity of the bio-oil varies from 25 cPoise up to 1000 cPoise depending on the water content, the amount of light compounds and the aging, and (3) the water content in bio-oils ranges typically between 14–33% by weight; this water cannot be removed by conventional methods like distillation as phase separation may occur above certain water contents (Demirbas and Balat, 2006).

Airey *et al.* (2008) stated that the characterization of the rheological properties of the materials is given primary emphasis in the measurement of physical properties of pavement binders, i.e. bitumen. Likely, rheological properties play a significant role in describing the behavior of bio-oils. Measuring the rheological properties is useful to determine behavioral and predictive information for bio-oils as well as knowledge of the effect of processing, formulation changes and aging phenomena. As a result, it is important to have theoretical knowledge as related to rheological aspects.

6. Background on bio-asphalt and its use in HMA

By definition, bio-oils can be described as dark brown, free-flowing organic liquids that are comprised mainly of highly oxygenated compounds (Mohan *et al.* 2006). In other words, it is the liquid produced from the rapid heating of biomass in vacuum condition. Bio-oils have many synonyms that can be listed as follows: pyrolysis oil, pyrolysis liquid, bio-crude oil (BCO), wood liquid, wood oil, liquid smoke, wood distillates, and pyroligneous acid (Mohan *et al.* 2006 and Oasmaa *et al.* 2005). Due to the variety of forestry and agricultural sources from which bio-oils are derived, bio-oils are a complex chemical mixture of water, guaiacols, catecols, syringols, vanillins, furancarboxaldehydes, isoeugenol, pyrones, acetic acid, formic acid, and other carboxylic acids. Also, bio-oils encompass other major groups of compounds, including hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids, and phenolics as reported by Mohan *et al.* (2006). As a result of the presence of cellulose, hemicellulose, and lignin in forestry and agricultural crops, the production of bio-oils can be described as the rapid and simultaneous depolymerization and fragmentation of these compounds while rapidly increasing temperature.

Currently, the state of the art for the utilization of bio-oils is concentrated on its use as biorenewable fuels to replace fossil fuels. However, there has been a limited amount of research investigating the applicability of bio-oils as a bitumen modifier or extender. Williams et al. 2009 conducted research on the usage of bio-oils fractions as an extender in original and polymer modified asphalt binders. They reported that the bio-oils can considerably increase the performance grade of polymer-modified asphalt binders by nearly 6°C. In addition, it was concluded that the effect of bio-oils was dependent upon many factors including the base asphalt, source of the biomass from which the bio-oils were derived, and the percentage of bio-oils blended with asphalt binders (Williams *et al.* 2009). Moreover, Williams et al. reported that up to 9% of a bio-oil could be blended with asphalt binders with significant improvement in the performance grade of the bio-oil modified asphalt binder. Fini and others have found that the use of swine manure-based biobinder as an asphalt modifier can enhance the asphalt low-temperature performance (Fini *et al.* 2010, You *et al.* 2011). Based on the conclusions of these investigations, the utilization of bio-oils as a bitumen modifier is very promising. Nevertheless, there has been no research conducted until recently that studies the applicability of using bio-oils as a bitumen substitute (100% replacement) to be used in the paving industry.

7. Current State of the Practice for Bio-oils

Bio-fuel production plants produce liquid co-products that are high in lignin content. Due to that, bio-oils have been used in many traditional uses which include but are not limited to concrete admixtures, binders, well drilling mud, dust control, vanillin production, and dispersants (Williams *et al.,* 2009). Lignin, which is a biological polymer, is known as an antioxidant compound due to the presence of large amounts of phenolic structures (Williams *et al.,* 2009). Due to the results of some investigations, it has been found that lignin can be utilized as an extender in asphalt to help reduce the use of petroleum with no adverse effects on performance (Raouf and Williams, 2010).

For asphalt pavements, oxidation can cause deterioration via long-term aging and eventually result in cracking. Therefore, bio-oil could potentially serve as an antioxidant additive in asphalt mixtures. The evaluation of the effects of lignin-containing bio-oil for utilization in asphalt binders, and attempt to optimize the bio-oil modification formula by adding other additives was the main objective of Tang's research 2010. Using bio-oil as an antioxidant in asphalt production could prove to be an economical alternative to conventional methods while being conscious of the environment and increasing the longevity and performance of asphalt pavements. Tang, (2010) was added Bio-oil to the asphalt binders in three different percentages by weight, 3%, 6%, and 9%. Moreover, tall oil fatty acids, which is a viscous yellow odorous liquid as a by-product obtained from the southern kraft pulping process, was introduced to optimize the bio-oil modified binders. In general, the corn stover, oak wood, and switch grass derived bio-oil indicate that there is potential to increase the high temperature performance of asphalt binders. However, the increase in high temperature performance adversely affects the low temperature binder properties.

Some other researchers have found that the use of swine manure-based bio-binder as an asphalt modifier can; 1) enhance the asphalt low-temperature performance, 2) improve fatigue cracking resistance, 3) decrease rutting resistance, and 4) reduce mixing and compaction temperatures by reducing the viscosity (Fini *et al.,* 2010*, and* You *et al.,* 2011).

Pan, (2013) has studied the anti-oxidation mechanisms of bio-based additives, using the coniferyl-alcohol lignin, by developing a quantum chemistry based chemophysical environment in which the various chemical reactions among asphalt components, anti-oxidative additive and oxygen, as well as the incurred physical changes. The techniques of X-ray photoelectron spectroscopy (XPS) was used to prove the validity of the modified and unmodified asphalt models, from which the XPS results showed high agreement to the model predictions.

Fini et al. (2013) have investigated the feasibility of the application of scrap tire and swine manure to produce a sustainable alternative for bituminous asphalt used in pavement construction to compare the rheological properties of Biomodified Rubber (BMR) with a crumb rubber–modified (CRM) binder. They found that the BMR has comparable properties with the CRM binder in terms of both shear susceptibility and temperature susceptibility. Furthermore, the introduction of the bio-binder into the CRM binder was beneficial in improving the low temperature property of the CRM binder while also reducing the CRM binder's overall viscosity which decreases energy consumption and overall construction cost.

Mills-Beale et al. (2014) have conducted a research to investigate the viability of using swine based bio-binder to improve the rheological properties of bituminous asphalt binder. They found that the addition of bio-oil to the base asphalt will: 1) Forms a homogenous polymeric mix with traditional asphalt binders; 2) Decreases the viscosity of the base binder; 3) Creates lower phase angle (δ) values and thus more elastic biomodified binders systems; 4) Decreases the Complex modulus (G^*) properties of the bio-modified binder compared with the control Performance Grade PG 64-22 binder; 5) At higher temperatures, the biomodified binder showed improved high-temperature rutting resistance performance; 6) Can improve the low-temperature cracking properties of asphalt binders and mixtures; 7) The chemical functional groups of the PG 64-22 binder remained unchanged even with the addition of the swine waste asphalt; and 8) The FTIR spectra proved the swine bio-binder decreased the stiffness of the PG 64-22 binder through the reduction in molecularcarbonyl and sulphoxide aging indexes investigations.

8. Rheological performances of bio oil

Yang *et al.,* (2013) have investigated the performance of asphalt binders modified by bio-oil generated from waste wood resources. They used three types of bio-oils generated from wood waste resources. The original bio-oil (OB), de-watered bio-oil (DWB) and polymer modified bio-oil (PMB). The three types were added into the base asphalt PG 58-28 at 5% and 10% by weight. The rotational viscometer (RV), dynamic shear rheometer (DSR), rolling thin film oven (RTFO), pressure aging vessel (PAV) and bending beam rheometer (BBR) were conducted to evaluate the rheological properties of bio-oil modified asphalt binders. The Superpave™ binder specification was used to evaluate the performance of bio-oil modified asphalt binders. They showed that the addition of bio-oil can lower the mixing temperature of asphalt mixtures while improve the high temperature performance of asphalt binders. However, the medium and low temperature performance was sacrificed. Comparison among the three types of bio-oil modified asphalt binders showed that PMB modified asphalt binders had the highest stiffness, followed by the DWB and OB. The OB had the lowest effect on the base asphalt binder compared to other two types of bio-oils.

Raouf and Williams, (2010) have revealed that the bio-oils cannot be used as biobinders/pavement materials without any heat pre-treatment/upgrading procedure due to the presence of water and volatile contents in considerable amounts. The heat treatment/upgrading procedure for deriving bio-binders from bio-oils should be determined for each type of bio-oil separately due to the significant difference between the different types of bio-oils, e.g. the chemical composition, the process by which the bio-oils were derived, and the type of the biorenewable resource from which the bio-oils were derived. They also showed that the temperature range of the viscous behavior for bio-oils may be lower than that of bitumen binders by about 30-40°C. The high temperature performance grade for the developed bio-binders may not vary significantly from the bitumen binders; however, the low temperature performance grade may vary significantly due to the high oxygen content in the bio-binders and subsequent aging compared to the bitumen binders.

Some researchers compared the rheological properties of conventional and polymer modified bitumens with binders derived from renewable resources (synthetic binders), i.e. triglyceride oils and carbohydrates. Their study was focused on the applicability of the utilization of binders derived from renewable resources as a viable bitumen replacement (Airey *et al.,* 2008).

Their investigations concluded that the synthetic binders were not showing the same rheological properties. For instance, one synthetic binder behaved as a "soft" 100/150 penetration grade while the other behaved as a "hard" 10/20 penetration grade. In addition, one of the binders showed very soft behavior, so they concluded that it cannot be used as an asphalt replacement but it can be used as a modifier for hard bitumen binders. Generally, synthetic binders displayed partly the same rheological properties compared to the conventional bitumen binders even though there were some differences in their temperature susceptibility. In addition, synthetic binders showed almost the same rheological properties compared to polymer modified bitumens in terms of their ability to switch between viscous and elastic dominated behavior as concluded by Airey *et al.* (2008).

Some researchers have determined some interesting, but only preliminary physical, chemical and physical characteristics of bio-asphalt produced from corn stover, switch grass and oak wood waste (Williams, 2009). These worth mentioning findings are that: 1) the addition of this type of bio-asphalt results in stiffening effect on petroleum-based asphalt binders; 2) The stiffening effect are dependent on the biomass source of bio-oil and amount of fractionated bio-oil; 3) the stiffening effect increases the high, intermediate and low critical temperatures of the asphalt-lignin blends, with the high temperatures increased more than the low temperatures. In terms of performance grade, the grade ranges in some combinations are increased by one grade (6ºC) and in other combinations no effects.

Raouf, (2010) found that the bio-binders developed from oakwood, switchgrass, and corn stover bio-oils cannot be treated at temperatures higher than 120°C because of the volatilization of some bio-oil compounds. Raouf, (2010) further found considerable differences between the properties of the bio-oils and asphalt at the same temperatures, and thus the Superpave test criterion should be modified to comply with the bio-binders properties, namely the Superpave specifications for the rolling thin film oven test (RTFOT) and the pressure aging vessel (PAV) procedures. Longer in-situ aging studies would need to be done to understand the aging mechanisms of biobinders such that simulative laboratory criteria can be established.

The Rotational Viscosity test is to determine the viscosity at high temperatures and furthermore the workability of asphalt binders. The RV test for virgin asphalt binder can determine the mixing and compaction temperatures of asphalt mixtures during the construction. The RV test in this study follows the standard AASHTO T 316 or ASTM 4402-02 [AASHTO 2011 and ASTM 4402-02] (Yang *et al.,* 2013).

Direct Shear Rheometer DSR test is to determine the visco-elastic property of asphalt binders in a broad range of temperatures and frequencies. The standard procedure of DSR test follows AASHTO T 315 [2008]. The DSR test is conducted for virgin, RTFO- and PAV- aged asphalt binders (Yang et al., 2013).

One of the main concerns of the application of bio-oil is the fast aging. To reduce the aging effect of bio-oil on the asphalt binder performance, one potential way is to reduce the short-term aging time, which will also require less construction time in the practice. The RTFOT temperature should be modified to 110°C to 120°C instead of 163°C to be consistent with the intended mixture production temperature. Also, a period of 20 min was established to be the duration that resembles the mixing duration. The RTFO test in this study followed the standard test specified in AASHTO T 240 [2009]. The asphalt binders are conditioned in the oven at 163°C for 85 minutes. The aging duration in the PAV should be shortened to 2.5 h instead of 20 h and the temperature of the degassing container should be lowered to 120°C instead of 170°C. The PAV test is to simulate the long term aging of asphalt binders during the service life. The PAV test in this study followed the standard test specified in

AASHTO R 28 [2009] (Yang et al., 2013). Raouf 2010 found that it was difficult to reach low-temperature grades of binders when attaining the appropriate high-temperature grades.

The BBR test is to investigate the low temperature performance (thermal cracking) of asphalt binders. The test procedure follows AASHTO T 313. The materials used in the BBR test are the PAV aged asphalt binders. The SuperpaveTM binder test recommends -18°C as the test temperature for PG 58-28. To better understand the low temperature performance of asphalt binders, -12°C was added as a second test temperature (Yang et al., 2013).

The high and low critical temperatures are the highest and lowest temperatures the asphalt binder can work at. They are determined by the DSR and BBR test, respectively. According to the Superpave™ specification, the $|G^*|/\sin\delta$ at 1.59 Hz (10 rad/s) should be higher than 2.2 kPa after RTFO aging, while the creep stiffness and m-value should be lower than 300 MPa and higher than 0.300, respectively. Thus, the high critical temperature is determined when the $|G^*|/\sin\delta$ at 1.59 Hz is equal to 2.2 kPa. The low critical temperature is determined when the creep stiffness (S) is and m-value just pass the requirement (Yang et al., 2013).

In many cases, the characteristics of asphalt binders need to be changed to improve their elastic properties at low temperatures for sufficient cracking resistance, and to increase its shearing resistance during sustained loads and high temperatures for rutting resistance. The physical properties of bitumen are typically modified with the addition of styrene-butadienestyrene (SBS) polymers to produce an improved asphalt grade that enhances the performance of asphalt paving mixtures. A viable alternative to using SBS polymers would be the use of recycled rubber from tires (Peralta *et al.*, 2012).

The Australian GEO320 MRH molasses-based asphalt bitumen prototype developed in line marking road projects have been used by The South Australian Roads and Traffic Authority (RTA) and the New South Wales counterparts (You *et al.,* 2012). It provided similar performance results comparable to Shell's CL320 residue bitumen which was used by the ARRB Transport Research in 2002. Preliminary results from this type of bio-asphalt suggests that the GEO320 MRH bioasphalt holds great potential in resisting pavement distresses like fatigue, solvent, cracking, rutting, and skidding. Their results also showed that this kind of asphalt is compatible with glass spheres (balotini) for reflecting light for night time road safety. It is also compatible with recycled plastics and reclaimed tire rubber and the coloring system which Ecopave™ research has developed is resistant to wear and weathering. In compacting asphalt paving mixtures, GEO320 MRH gives the mixture low compaction properties, just like Warm Mix Asphalt.

8.1. Temperature Susceptibility of bio oil

Temperature plays a major role in changing the viscosity of bio-oils. In addition, the reduction in viscosity's measurement due to temperature is more significant as compared to shear rate. Explicitly, the viscosity of a bio-oil is reduced rapidly as the temperature increases, and then, the bio-oil's viscosity started to display temperature independence effect.

Temperature susceptibility, as defined by Roberts *et al.* (1996), is the rate at which the consistency of a binder changes with a change in temperature. The temperature susceptibility of a binder is a very crucial property as binders having high susceptibility to temperature are not desired or required for two reasons. First, at high temperatures, their viscosity can be very low resulting in mixing problems during compaction. Second, at low temperatures, their viscosities can be very high resulting in low temperature shrinkage cracking. Due to the change in the behavior as a result of changing temperature, the behavior of a paving binder should be studied at three different temperatures, e.g. high, intermediate and low.

Asphalt binder or bitumen, as an example, has three different behaviors due to the change in temperature. At high temperatures or under sustained loads (slow moving or parked trucks), an asphalt binder behaves like a viscous liquid. At intermediate temperatures, an asphalt binder displays the characteristics of both viscous and elastic solids. At low temperatures or under rapidly-applied loads (e.g. fast moving trucks), an asphalt binder behaves like an elastic solid. Elastic solids can be described as rubber bands which deform when loaded and return to their original shape when unloaded. Due to this range of behavior, asphalt binder is an excellent adhesive material to be used as a paving material. For example, asphalt binder when heated acts like a lubricant so it facilitates the process of mixing, coating and compaction of binder with aggregates to form a smooth and dense surface. On the other hand, asphalt binder when cooled acts like a glue to hold the aggregate together in a solid matrix (Raouf and Williams, 2010).

8.2. Age Hardening or oxidation of bio oil

A basic assumption built into the rolling thin film oven (RTFO) and pressure aging vessel (PAV) procedures is that asphalt will exhibit consistent aging behavior and that aging will have a predictable effect on the performance in mixtures and pavements. Consequently, RTFO and PAV may not adequately represent plant and field aging. RTFO should be run over a range of times and temperatures to see if normal time–temperature correlations still hold. The same applies for PAV. Run PAV at 60°C for extended times and compare the resulting behavior to the results at standard conditions (Kluttz, 2012).

Since the bio-oils are chemically organic, they react with oxygen from the environment and this kind of reaction is called "oxidation", which can change the structure and the composition of the bio-oil. Oxidation can cause the material to become more brittle (stiffer), which leads to the term oxidative or age hardening. Aging occurs at a slower rate in a pavement, but this rate increases in warmer climates. Age hardening is considered to be one of the most important factors that leads to the change in the rheological properties (Raouf and Williams, 2010).

As reported by Mohan *et al.* (2006), the viscosity of bio-oils increases due to the aging effect. Temperature is the most driving variable that leads to the aging effect, and hence the viscosity of the bio-oils. In addition, some phase separation may also happen. As a result, instability problems may arise that are believed to result from a breakdown in the stabilized microemulsion and to chemical reactions, which continue to proceed in the bio-oils (Mohan *et al.,* 2006).

The amount of aging that occurred in binder during production and in service can be quantified in terms of viscosity as the Aging Index "AI" as shown in Equation 1 (Roberts *et al.,* 1996). This aging index has been employed to evaluate relative aging of asphalt cements of different grades and/or from different sources.

$$\text{aging Index} = \frac{\text{Viscosity of Aged Binder}}{\text{Viscosity of Original Binder}} \qquad (1)$$

9. Mechanical behavior of bio-asphalt mixtures:

The laboratory evaluation of asphalt mixtures containing bio-binder technology was the main objective of many researches. A suite of laboratory tests was conducted by Mohammad et al. (2013) to capture the mechanistic behavior of the mixtures against major distresses. Laboratory testing evaluated the rutting performance, moisture resistance, and fracture resistance of the produced mixtures using the Hamburg loaded-wheel tester, the modified Lottman test, the semi-circular bending (SCB) test, and the thermal stress restrained specimen (TSRST) test. Results of this research showed that mixtures modified with bio-binder had similar or improved rutting performance when compared to the conventional mixes. With respect to moisture susceptibility, most mixtures exceeded the 80% tensile strength ratio. In addition, mixtures containing bio-binder exhibited reduced fracture resistance as compared to conventional mixes and bio-binder modification improved the low temperature fracture performance of the mixtures when compared to conventional mixtures of similar performance grade (Mohammad et al., 2013).

Yang et al., (2013) have investigated the performance of binders modified by bio-oils generated from waste wood resources using three types of bio-oils: the Original Bio-oil (OB), Dewatered Bio-oil (DWB), and Polymer Modified Bio-oil (PMB). Asphalt Pavement Analyzer (APA), Tensile Strength Ratio (TSR), Four Point Beam Fatigue and Dynamic Modulus (E*) were conducted for the mechanical performance evaluation of asphalt mixtures modified by bio oil. The results showed that: 1) the dynamic modulus (|E*|) of some OB and DWB modified asphalt mixtures were slightly lower than that of the control asphalt mixture while the |E*| of PMB modified asphalt mixtures were higher than that of the control asphalt mixture; 2) the rutting depth of most of the bio oil modified asphalt mixtures were slightly higher than that of the control asphalt mixture; 3) most of the bio oil modified asphalt mixtures had higher fatigue lives than the control asphalt mixture; 4) the control asphalt mixture and 5% bio oil modified asphalt mixture had higher TSR value than that of the 10% bio oil modified asphalt mixtures (Yang et al., 2013).

10. Conclusions and summary

Recycling of waste materials in highway construction should be encouraged. However, it is necessary to address the engineering concerns, environmental concerns and economic concerns mentioned in this paper before any large scale use of these materials. HMA containing bio-oil material should perform as well or better than conventional HMA. It should also be environmentally safe both for the first construction and future recyclability.

Bio-asphalt is an opportunity for the asphalt industry to improve its product performance, construction efficiency, and environmental stewardship. Studies have shown that the performance characteristics of bio-asphalt mixes can be at least equivalent to conventional mixes. This is possible because of the often better workability and hence better compaction which can be achieved with their use. The lower production temperature also reduces the ageing of the bitumen during the production stage, which results in an improved thermal and fatigue cracking resistance. All these factors lead to benefits in different aspects, such as environmental impact, paving operations, worker health and safety, and economic cost effectiveness.

Generally speaking, authors claim that the use of bio-oil in HMA have a significant number of advantages, basically associated with energy saving which lead to a major reduction of greenhouse gasses (GHG) emissions and pollutants as well as paving and production benefits. Even though some drawbacks have also been pointed out, benefits of the using bio-oil in a whole seem to surmount their drawbacks.

In summary, it is clear from the foregoing that the performance of the asphalt mixture after adding bio-oil depends largely on the chemical composition of the source biomass as well as on the method it may be produced by, and to note the discrepancy in the test results and contradiction between the findings of the earlier researchers in this field. Thus, it is worth to continue in research to find out more about the modification of asphalt mixtures by adding bio-oil using locally produced materials after studying their properties thoroughly as empty frond bunch of oil palm tree due its abundance.

11. Current challenges and Future Efforts

In many previous studies, researchers have conducted series of tests to evaluate the compatibility of bio oil and petroleum-based asphalt, the rheological properties of bio-asphalt and the mechanical performances of bio-asphalt mixtures. However, the chemical mechanism during bio oil aging and how to simulate the short-term and long-term aging are the two main obstacles for the better use of bioasphalt.

Firstly, to reveal the inherent chemical mechanism of bio oil aging can present full explanation for the test results and further, to find ways to control the aging in a proper level. For instance, different chemical reactions that result in different rheological properties may occur at different temperatures. If these chemical reactions can be well understood, better ways to deal with the bio-asphalt can be found.

Secondly, the standard RTFO and PAV aging are not suitable for bio-asphalt, especially that with high percent of bio oil, because of the faster aging of bio oil. The short-term aging simulation can make guidance on the practical work of mixing and compaction. For example, the construction time and temperature should be reduced to avoid over aging of the bio-asphalt. Theoretically, bio-asphalt with different bio oil percentage should result in different construction time and temperatures to get the same aging level. Thus, Thus, to find proper ways to simulate short-term and long-term aging for bio-asphalt is very important for the application of bio-asphalt.

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