Effect of fast pyrolysis bio-oil from palm oil empty fruit bunch on bitumen properties

Chia Chin Poh, Norhidayah Abdul Hassan, Noor Azah Abdul Raman, Nurul Athma Mohd Shukry, Muhammad Naqiuddin Mohd Warid, Mohd Khairul Idham Mohd Satar, Che Ros Ismail, Sitti Asmah Hassan and Nordiana Mashros
Faculty of Civil Engineering, Universiti Teknologi Malaysia, Johor, Malaysia
E-mail: hnorhidayah@utm.my

Abstract. Bitumen shortage has triggered the exploration of another alternative waste material that can be blended with conventional bitumen. This study presents the performance of pyrolysis bio-oil from palm oil empty fruit bunch (EFB) as an alternative binder in modified bitumen mixtures. The palm oil EFB was first pyrolyzed using auger pyrolyzer to extract the bio-oil. Conventional bitumen 80/100 penetration grade was used as a control sample and compared with samples that were modified with different percentages, i.e., 5% and 10%, of pyrolysis EFB bio-oil. The physical and rheological properties of the control and modified bitumen samples were investigated using penetration, softening point, viscosity and dynamic shear rheometer (DSR) tests. Results showed that the addition of EFB bio-oil softened the bitumen with high penetration and a reduction in softening point, penetration index, and viscosity. However, the DSR results showed a comparable rutting resistance between the bitumen samples containing EFB bio-oil and virgin bitumen with a failure temperature achieved greater than 64°C.

1. Introduction
The increased demand for crude oil due to the increasing number of automobiles has significantly reduced the crude oil reserves worldwide. This phenomenon resulted in the increased price of bitumen. Thus, many experts attempt to develop economically and environmentally sustainable methods using alternative binders that are suitable for hot mix asphalt. Challenges are also faced by contractors involved in the road construction industry because of the continuous price fluctuation of crude oil due to its low availability and high demand. Bitumen is a viscoelastic material manufactured through the distillation of crude oil in refineries and has been widely used for the construction of asphalt pavement worldwide. The physical properties of bitumen are influenced by its chemical composition, which consists of high-molecular-weight hydrocarbons with some functional groups containing sulfur, nitrogen, and oxygen atoms [1]. In practice, the properties of bitumen change during its service life because of high axle load and extreme environmental effects, such as acid rain, chemical attack, and high surrounding temperatures. Repeated loads from the increased vehicle loads will affect the strength of pavement due to fatigue. Exposure to high temperature will gradually soften the bitumen with low stiffness, thereby becoming susceptible to permanent deformation. These issues have been evident for the last three decades. Pavement research has been facing more demands than before and thus requires the enhancement of the properties of bituminous materials.
Given that the performance of road pavement is mainly affected by the properties of bituminous binder, conventional bitumen often cannot provide the desired resistance to pavement distresses [2]. The use of modified bitumen is an important solution to change the properties of conventional bitumen and sustain the durability of the pavement. Some of these properties include elasticity and adhesive or cohesive strength. Modified bitumen currently has various applications, and bituminous binder has been improved by using various kinds of alternative materials. Polymers are the most commonly used modifying agents that can be effectively used as bitumen modifier. Different types of polymers, including polyethylene, polypropylene, styrene butadiene styrene, styrene butadiene rubber, have been described in previous investigations [3-6]. The potential utilization of various by-products in road construction has been recently investigated. The use of recycled materials, such as tire rubber, plastic wastes, waste engine oil, and cooking oil, as alternative binder modifiers has also been studied [7-11]. Agricultural waste products, such as oil palm fruit ash, palm oil fuel ash, and coconut shell charcoal ash, have also been used as alternative bitumen modifiers by taking advantage of the abundance of waste by-products from palm oil mill industry to help reduce environmental pollution [12-14]. The modification of bitumen with various additives offers several benefits, including improved stiffness at high temperature, cracking resistance at low temperatures, moisture resistance, fatigue life, rutting performance, and decrease in temperature susceptibility. Nanomaterials are widely utilized to improve the performance of asphalt pavement, especially for the modification of bitumen for flexible pavements. Various types of nanomaterials, such as nanoclay, nanosilica, and carbon nanotubes, were studied to reveal their effectiveness in improving the engineering properties of bitumen and mixture [15-17].

The bio-oil extruded from biomass resources, such as oakwood, switchgrass, rice husk, oil palm, and coconut shell, shows significant potential as a bitumen modifier because this bio-oil possesses similar chemical properties with petroleum binders [18]. Among the current technologies, thermochemical conversion processes, such as pyrolysis, gasification, and liquefaction, are the most commonly used to convert biomass materials into sustainable bio-oils [19]. Heating organic materials at high temperature in the absence of oxygen and consequently producing solids, bio-oil, and gases are basically a thermochemical process [20]. Pyrolysis processes are mainly classified into carbonization (very slow), conventional (slow), fast, and flash depending on the operating conditions. Slow pyrolysis is used primarily for charcoal or char production, whereas fast pyrolysis is mainly used to maximize the production of liquid or bio-oil [21]. Fast pyrolysis consists of four main features that help increase the liquid yield; these features include high heating rate, monitoring of reaction temperature in the range of 425 °C to 600 °C, short vapor residence times of less than 3 s, and rapid cooling of the product gas to produce bio oils [22]. These processes yield approximately 75 wt% of liquid bio-oils, 10 wt% to 15 wt% biochar, and 10 wt% to 15 wt% of condensable gases [23]. Bio-oils or pyrolysis oil are dark-brown, free-flowing liquids that are composed of several hundred organic compounds, mainly including acids, alcohols, aldehydes, esters, ketones, phenols, and lignin-derived oligomers [24]. Bio-oil has significantly high moisture content that usually varies from 15% to 30%, thereby contributing to its low viscosity and the difficulty of obtaining homogeneous samples from these bio-oils. The presence of water in biomass reduces the high heating value of bio-oil to below 19 MJ/kg as compared with 42 MJ/kg for conventional petroleum oil. This factor limits the application of bio-oil as a bitumen substitute in paving industry. The high water content of bio-oil can cause spontaneous phase separation, which will then lead to ignition and combustion problems and thus poor quality. This phenomenon will influence the behavior of bio-oil during pyrolysis and affect the physical properties and quality of the pyrolysis liquid [25]. Thus, the phase stability of bio-oil must be improved by reducing the water content and the aging of contributing light components, such as volatile aldehydes and ketones prior to pyrolysis to ensure the high quality and energy value of the bio-oil [26,27].

Yang et al. [28] investigated the performance of modified bitumen with bio-oil extracted through pyrolysis from waste wood materials. Three different types of bio-oils, namely, polymer-modified bio-oil (PMB), de-watered bio-oil (DWB) and original bio-oil (OB), were used as additives at 5% and 10% by weight into the virgin bitumen. Their study indicated that the addition of bio-oil improved the
high temperature performance and lowered the mixing temperature of asphalt mixtures. The results also showed that OB-modified bitumen binders had the lowest stiffness, whereas the DWB- and PMB-modified bitumen binders had moderate and highest stiffness, respectively. Mohammad et al. [29] conducted a comprehensive laboratory investigation of asphalt mixtures containing bio-binder technology. Their findings showed that mixtures modified with bio-binder showed improved rutting resistance performance as compared with conventional mixtures. In addition, the mixtures containing bio-binder exhibited improved low temperature fracture performance and a tensile strength ratio of more than 80% in the moisture susceptibility test. Mills–Beale et al. [30] investigated the effect of the addition of bio-binder from swine manure on the rheological properties of bio-bitumen mixtures. Their results showed that bio-modified bitumen had low viscosity and improved thermal cracking performance as compared with conventional bitumen. Fini et al. [31] also reported that the swine manure-based bio-bitumen mixtures showed improvements in fatigue cracking resistance, rutting resistance, and low mixing and compacting temperature, which are attributed to the reduction in binder viscosity.

The bio-oil benefits the performance grade of bitumen only when the proper amount is blended or replaced into the conventional bitumen. On the contrary, the utilization of bio-binders derived from the biomass is advantageous because the materials are inexpensive and easily available. These materials can be used by existing asphalt industries to manage problems related to the availability and price of crude oil. The application of bio-oils for the modification of bitumen can improve the performance of asphalt pavements. Therefore, this study aims to investigate the physical and rheological properties of bitumen modified with bio-oils. Fast pyrolysis was conducted to extract the bio-oil from palm oil empty fruit bunch (EFB). The physical and rheological properties of the control and modified bitumen samples were investigated using penetration, softening point, viscosity, and dynamic shear rheometer (DSR) tests.

2. Experimental

2.1. Materials

The bio-oil used in this study was extracted from palm oil EFB through fast pyrolysis. Figure 1 shows the unprocessed and processed palm oil EFB for recycling of palm oil waste. This process involves a series of steps that included the extraction and subsequent purification of the bio-oil. Purification was conducted to remove the water content from the pyrolysis bio-oil, which usually contains a significant amount of condensed water due to the moisture of biomass materials. Elemental investigation of bio-oil was conducted using Automated CHNS Analyzer to determine the chemical composition of carbon (C), hydrogen (H), nitrogen (N), and Sulfur (S). Table 1 shows the comparison of the elemental analysis of pyrolysis EFB bio-oil and of virgin bitumen 80/100. Compared with that for virgin bitumen 80/100, the significantly low percentage by weight of C and H for pyrolysis EFB bio-oil indicates that this bio-oil contains less fraction of long-chain hydrocarbon, which leads to its soft behavior and low stiffness properties. The high sulfur content of bio-oil contributes to the binder viscosity reduction and significantly improves the workability of the mix. This characteristic allows the asphalt mixture to be prepared and compacted at low temperatures, resulting in low energy consumption [32]. For the sample preparation, bitumen with penetration grade 80/100 was used to blend with bio-oils at 140 °C. During asphalt modification, bio-oil was added at 5% and 10% by weight of the control sample. The mixture was blended properly by using high shear mixer at a constant speed of 1000 rpm for 1 h at 140 °C until it was uniformly mixed.
2.2. Laboratory tests

2.2.1. Penetration. Penetration test was performed to determine the consistency of the modified bitumen sample. This test was conducted by determining the distance in tenths of a millimeter using a standard needle penetrated vertically into a sample of the material under fixed conditions of temperature, load, and time. The bitumen sample was heated and stirred until it became sufficiently fluid and then poured into a penetration cup. The sample was cooled at room temperature for an hour and then placed in a water bath for another hour at 25 °C. The penetration equipment was used to perform the test with the applied load of 100 g for 5 s at a temperature of 25 °C. The test was performed by placing the penetrometer outside the bath and in the transfer dish to maintain the temperature. Penetration index (PI) was calculated to measure the temperature sensitivity of bitumen. High PI corresponds to low temperature sensitivity, whereas low PI corresponds to great temperature sensitivity, indicating that the binder tends to change its consistency faster than the temperature change.

2.2.2. Softening point. Softening point test was conducted to determine the softening temperature of bitumen by using ring and ball apparatus. In this test, the heated modified bitumen sample was poured into rings and then cooled at room temperature for 30 min. The excess sample was removed with warm blade to ensure that the test specimens were leveled with the top of the rings. The filled rings were placed in the ring holder, whereas the ball-centering guide was positioned on the rings. In brief, 3.5 g of steel balls were placed on each sample. With the distilled water in the bath at 5 ± 2 °C, the assembled apparatus and steel balls were transferred to the liquid bath. The samples were heated, and the temperature at which the ball touches the base plate was recorded.

2.2.3. Viscosity. This test was conducted using rotational viscometer to determine the resistance to the flow of bitumen. The rotational viscometer determines the torque required to rotate a spindle at constant speed while immersed in the modified bitumen sample. The desired dynamic viscosity value, which is proportional to this measured torque, will eventually be obtained. When conducting the test, the spindle, sample chamber, and viscometer environmental chamber were first preheated to 135 °C. The modified bitumen sample was heated until it became fluid enough to be poured and was then
brought to the test temperature of 135 °C within approximately 30 min. Viscosity was reported as the average of three readings. The test was then repeated with temperature of 165 °C.

2.2.4. Dynamic shear rheometer (DSR). DSR involves a parallel plate rheometer that is used to apply shear strain or shear stress under a controlled temperature and frequency. This equipment is used to characterize the viscous and elastic behavior of asphalt at high and intermediate service temperatures. These characteristics can be used to evaluate the rutting and fatigue cracking potential of pavement. In this test, the bitumen sample was preheated until the binder became sufficiently fluid for easy pouring. The bitumen sample was then placed between the test plates of 25 mm diameter with 1 mm height as shown in Figure 2. The test was started after the sample had the desired temperature for at least 10 min. The DSR conditioned the sample for 10 cycles at a frequency of 10 rad/s (1.59 Hz). Thus, the machine gives the value of complex modulus (G*) and phase angle (δ) of the binder at a desired temperature and loading frequency.

![Figure 2. Dynamic shear rheometer (DSR) test.](image)

3. Results and discussion

3.1. Penetration and softening point

Figure 3 shows the result of penetration values, softening point, and PI of the bio-oil-modified bitumen. The different bitumen samples had increased penetration values and became soft with the increasing percentage of EFB bio-oil content. The 5% addition of bio-oil resulted in slightly higher penetration value of 90.5 PEN than that of the virgin bitumen at 86.9 PEN. This finding indicated that modification using up to 5% bio-oil on virgin bitumen can still achieve the target binder range in penetration grade of 80/100. For the addition of 10% bio-oil, the penetration value increased up to a maximum of 112.4 PEN. This property would be useful in obtaining soft, modified bitumen by blending the EFB bio-oil into hard-grade bitumen. The soft bitumen is suitable for use in cold climate region. This application agrees with the results obtained by Airey and Mohammed [33], who reported that bio-binders exhibit soft behavior and are more suitable to be used as a modifier for stiffer-grade bitumen rather than as a replacement. Furthermore, the softening temperature of bitumen decreased when the EFB bio-oil content increased, indicating that bitumen became susceptible to temperature change when the EFB bio-oil content increased. The PI variation was reduced from −2.52 for virgin bitumen to −9.86 for 10% of EFB bio-oil-modified bitumen. Therefore, the high content of EFB bio-oil significantly affected the bitumen susceptibility to temperature changes.
3.2. Viscosity
The viscosity test result of virgin bitumen grade 80/100 PEN and EFB bio-oil-modified bitumen at 135 °C and 165 °C are shown in Figure 4. Modified bitumen with the addition of 5% and 10% of EFB bio-oils achieved lower viscosity than the virgin bitumen. At the temperature of 135 °C, the virgin bitumen showed the viscosity value of 0.47 Pa.s, whereas the modified bitumen with 5% and 10% EFB bio-oils exhibited the same viscosity value of 0.40 Pa.s. This indicates that the viscosity value of bitumen decreases slightly with the increasing bio-oil content, indicating that bio-oil-modified bitumen has lower resistance to flow and small internal friction compared to the virgin bitumen. This phenomenon occurs because the bio-oil is less viscous, thus acting as a lubricant that contributes to the low internal friction. At the temperature of 165 °C, the viscosity of virgin bitumen remained higher but comparable to those with bio-oil at 0.13 Pa.s and 0.1 Pa.s respectively. This finding implies that temperature influences the viscosity reduction for virgin and modified bitumen samples.
3.3. Rutting resistance
DSR test was conducted to measure the rutting resistance of bitumen when $G^*/\sin \delta$ is greater than 1.0 kPa. Based on Superpave specifications, the values of $G^*$ and $\delta$ obtained from DSR test were used as predictors of rutting (permanent deformation) temperature. Figure 5 shows the results of rutting resistance for the virgin and bio-oil-modified bitumen samples at five different temperatures (46 °C, 52 °C, 58 °C, 64 °C, and 70 °C). The result shows that the minimum value of $G^*/\sin \delta$ was obtained by the 5% bio-oil, and the virgin bitumen grade 80/100 PEN had the highest value of $G^*/\sin \delta$. The $G^*/\sin \delta$ values were incrementally decreased when the test temperatures increased. Furthermore, the $G^*/\sin \delta$ values increased when the percentage of bio-oil increased from 5% to 10%. The increase in concentration of bio-oil consequently increased the $G^*/\sin \delta$ values, indicating a good rutting resistance.

3.4. Failure temperature
According to Superpave specification, the failure temperature of a bitumen is defined as the temperature when the ratio of $G^*/\sin \delta$ is less than 1.0 kPa. High failure temperature values indicate
that the binders are less susceptible to permanent deformation at high pavement temperature. From the rheological data plot as in Figure 5, the failure temperature was selected at the rutting resistance of 1.0 kPa. Figure 6 shows the failure temperatures of virgin and bio-oil-modified bitumen samples. It is clearly shown that all bitumen samples have the failure temperatures greater than 64°C and less than 70 °C. The virgin bitumen and modified bitumen with 5% and 10% bio-oil have comparable failure temperatures of around 68 °C, 66 °C, and 67 °C, respectively. This finding indicated that the addition of bio-oil has slightly reduced the failure temperature of the bitumen compared to the virgin bitumen. However, an interesting highlight can be made on the bio-oil’s ability to give similar performance as the virgin binder under rutting condition particularly at high temperature even though its physical properties showed bio-oil soften the bitumen.

![Figure 6](image_url)

**Figure 6.** Failure temperature of asphalt binder with different percentages of bio-oil.

4. Conclusion
The findings conclude that adding EFB bio-oil at different percentages affects the temperature susceptibility of the bitumen. When the EFB bio-oil content is increased from 5% to 10%, the penetration value increases significantly, but the softening point and PI values of modified bitumen decrease drastically. The viscosity value of bitumen sample decreases when the EFB bio-oil content is increased, indicating that the modified bitumen has low internal friction and resistance to flow. According to the results of rutting parameter, high content of EFB bio-oil improves the rutting resistance of bitumen at high temperatures and gives a comparable result to the virgin bitumen.

Acknowledgements
The support provided by Malaysian Ministry of Higher Education (MOHE) and Universiti Teknologi Malaysia (research grant no. Q.J130000.2522.11H76 and R.J130000.7822.4F436) for this study is highly appreciated.

References
[1] Weigel S and Stephan D 2017 Relationship between the chemistry and the physical properties of bitumen Road Materials and Pavement Design (2017)015
[2] Ali A H, Mashaan N S and Karim M R 2013 Investigations of physical and rheological properties of aged rubberized bitumen Advances in Materials Science and Engineering (2013)007
[3] Polacco G, Berlincioni S, Biondi D, Stastna J and Zanzotto L 2005 Asphalt modification with different polyethylene-based polymers European Polymer Journal 41 (12) 2831–44
[4] Al-Hadidy A I and Yi-qiu T 2009 Effect of polyethylene on life of flexible pavements. *Construction and Building Materials* 23 1456–64

[5] Baochang Z, Man X, Dewen Z, Huixuan Z and Baoyan Z 2009 The effect of styrene–butadiene–rubber/montmorillonite modification on the characteristics and properties of asphalt. *Construction and Building Materials* 23 (10) 3112–17

[6] Kök B V and Çolak H 2011 Laboratory comparison of the crumb-rubber and SBS modified bitumen and hot mix asphalt. *Construction and Building Materials* 25 3204–12

[7] Tunçan M, Tunçan A and Çetin A 2003 The use of waste materials in asphalt concrete mixtures. *Waste Management & Research* 21 (2) 83–92

[8] Mahrez A and Karim M R 2010 Rheological evaluation of bituminous binder modified with waste plastic material. 5th International Symposium on Hydrocarbons & Chemistry (ISHC) May 23–25 Sidi Fredj, Algiers

[9] Kamaruddin N H M, Hainin M R, Hassan N A and Abdullah M E 2014 Rutting evaluation of aged binder containing waste engine oil. *Advanced Materials Research* 911 405–9

[10] Hainin M R, Aziz M M A, Adnan A M, Hassan N A, Jaya R P, Liu H Y 2015 Performance of modified asphalt binder with tire rubber powder. *Jurnal Teknologi* 73 (4) 55–60

[11] Azahar W N A W, Jaya R P, Hainin M R, Bujang M and Ngadi N 2016 Chemical modification of waste cooking oil to improve the physical and rheological properties of asphalt binder. *Construction and Building Materials* 126 218–26

[12] Rusbintardjjo G, Hainin M R and Yusoff N I M 2013 Fundamental and rheological properties of oil palm fruit ash modified bitumen. *Construction and Building Materials* 49 702–11

[13] Hainin M R, Jaya R P, Ali Akbar N A, Jayanti D S and Yusoff N I M 2014 Influence of palm oil fuel ash as a modifier on bitumen to improve aging resistance. *Journal of Engineering Research* 2 (1) 34–46

[14] Abdullah M E, Rosni N N M, Jaya R P, Yaacob H, Hassan N A and Agussabti 2017 Effect of charcoal ash coconut shell from waste material at different size on the physical properties of bitumen. *Key Engineering Materials* 744 121–5

[15] Yang J and Tighe S 2013 A review of advances of nanotechnology in asphalt mixtures. *Procedia-Social and Behavioral Sciences* 96 1269–76

[16] Abdullah M E, Zamhari K A, Buhari R, Kamaruddin N H M, Nayan N, Hainin M R, Hassan N A, Jaya R P and Yusoff N I M 2015 A review on the exploration of nanomaterials application in pavement engineering. *Journal Teknologi* 73 (4) 69–76

[17] Alhamali D I, Wu J, Liu Q, Hassan N A, Yusoff N I M and Ali S I A 2016 Physical and rheological characteristics of polymer modified bitumen with nanosilica particles. *Arabian Journal for Science and Engineering* 41 (4) 1521–30

[18] Mamat R, Hainin M R, Hassan N A, Rahman N A A, Warid M N M and Idham M K 2015 A review of performance asphalt mixtures using bio-binder as alternative binder. *Journal Teknologi* 77 (23) 17–20

[19] Wiedner K, Rumpel C, Steiner C, Pozzi A, Maas R and Glaser B 2013 Chemical evaluation of chars produced by thermochemical conversion (gasification, pyrolysis and hydrothermal carbonization) of agro-industrial biomass on a commercial scale. *Biomass and Bioenergy* 59 264–78

[20] Raman N A A, Hainin M R, Hassan N A and Ani F A 2015 A review on the application of bio-oil as an additive for asphalt. *Journal Teknologi* 72 (5) 105–10

[21] Basu P 2010 *Biomass gasification and pyrolysis: Practical design and theory* Technology & Engineering (Academic Press)

[22] Ward J, Rasul M G and Bhuiya M M K 2014 Energy recovery from biomass by fast pyrolysis. *Procedia Engineering* 90 669–74

[23] Bridgewater A V, Meier D and Radlein D 1999 An overview of fast pyrolysis of biomass. *Organic Geochemistry* 30 (12) 1479–93
[24] Xiu S and Shahbazi A 2012 Bio-oil production and upgrading research: A review Renewable and Sustainable Energy Reviews 16 (7) 4406–14
[25] Demirbas A 2009 Thermochemical conversion processes Biofuels Green Energy and Technology (London: Springer) pp 261–304
[26] Metwally M A R M 2010 Development of non-petroleum binders derived from fast pyrolysis bio-oils for use in flexible pavement PhD Thesis Iowa State University
[27] Venderbosch R H and Prins W 2011 Fast pyrolysis Thermochemical Processing of Biomass: Conversion into Fuels, Chemicals and Power, ed R C Brown (John Wiley & Sons, Ltd) pp 124–156
[28] Yang X, You Z and Dai Q 2013 Performance evaluation of asphalt binder modified by bio-oil generated from waste wood resources International Journal of Pavement Research and Technology 6 (4) 431–9
[29] Mohammad L N, Elseifi M, Cooper III S B, Challa H and Naidoo P 2013 Laboratory evaluation of asphalt mixtures containing bio-binder technologies Transport Research Record: Journal of the Transportation Research Board. 2371 58–65
[30] Mills-Beale J, You Z, Fini E, Zada B, Lee C H and Yap Y K 2014 Aging influence on rheology properties of petroleum-based asphalt modified with bio-binder Journal of Materials in Civil Engineering 26 (2) 358–66
[31] Fini E H, Oldham D J and Abu-Lebdeh T 2013 Synthesis and characterization of biomodified rubber asphalt: Sustainable waste management solution for scrap tire and swine manure. Journal of Environmental Engineering 139 (12) 1454–61
[32] Gawel I 2000 Sulphur-modified asphalts Asphaltenes and Asphalts, 2 vol 40B, ed T F Yen and G V Chilingarian (Netherland: Elsevier) pp 515–535