

A Review on the Application of Bio-oil as an Additive for Asphalt

Noor Azah Abdul Raman^a, Mohd Rosli Hainin^{a*}, Norhidayah Abdul Hassan^a, Farid Nasir Ani^b

^aFaculty of Civil Engineering, 81310 UTM Johor Bahru, Johor, Malaysia

^bFaculty of Mechanical Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

*Corresponding author: mrosli@utm.my

Article history

Received : 15 August 2014
Received in revised form :
15 October 2014
Accepted : 15 November 2014

Graphical abstract



Abstract

The rising cost of crude oil affects the asphalt paving industries and this in turn has encouraged researcher to modify or replace asphalt. The numbers of commercial vehicles increase every year. Hence, design, construction and maintenance of asphalt road facilities must be improved in order to provide the highest standards of safety and comfort, but certain areas of the road need some extra attention due to higher stressed than the others. For that reason road paving industry is interested in utilizing alternative and sustainable binder materials for modified asphalt to improve the production, placement and performance of asphalt mixtures. Nonetheless, sources of materials should be considered economically and environmentally viable after applying in pavement. According to previous research, the non crude petroleum binder was derived from the production of bio-oil through fast pyrolysis of biomass. The main source of bio-oil is from biomass industry or renewable organic industry such as timber waste, oil palm waste, rice husk, coconut trunk fibers, municipal waste and sugar cane waste. Alternatively, the bio-oil can be as substitute material as modification of asphalt. This paper presents a review of the source, characterization of bio-oil and the effects of bio-oil on the properties of asphalt.

Keywords: Asphalt; biomass; pyrolysis; bio-oil; blends

© 2015 Penerbit UTM Press. All rights reserved.

1.0 INTRODUCTION

The application of bio-oil could improve asphalt binder properties while reducing asphalt paving construction cost. Crude oil is the large amount source quantum of the fuel and supplying an almost quarter of the world's energy demands for the needs of industry as an aspiration to develop the nations. When a barrel of crude oil is pre-defined, around 40–50 percent is being applied to produce petrol (gasoline), with a fruitful reminder as a better suited to produce an abstracted crude ingredients such as diesel, heating oil's and jet fuel (kerosene), heavy bitumen, as well as the petrochemicals used to produce dyes, synthetic detergents and plastics [1]. Generally asphalt used by the paving industries today is obtained by processing the crude oils. The price of the crude oil is influenced by the demand on the different grade of crude oil. The demanding of the crude oil itself has accordingly changed the price per barrel and increased the energy costs in asphalt pavement.

Alternative binder predominantly is a better way to reduce the conventional bituminous binders that recently being applied for the pavement of materials which was derived from the fossil fuels. Converting biomass (plants and other organic waste) into sustainable and low carbon products could possibly replace the existing petroleum products. Bio-oil extruded from biomass is a renewable source of fuel from bio conversion that can be blended into the conventional bitumen as a modified binder. Using bio-oil modified binder in asphalt pavements could also reduce mixing

time, compaction temperatures, ageing and stiffening characteristics of the reclaimed asphalt pavements (RAPs) and virgin binders [2]. For this reason, more research needed to evaluate the material performance on the fundamental physical and chemical properties of asphalt [3]. Hot Mix Asphalt mixture performance tests indicated that the addition of bio asphalt to the mix can reduce the stiffness of the mixtures (dynamic modulus) and its resistance to rutting and fatigue cracking. Besides that, it also can increase the resistance to thermal cracking [4]. The construction of roadway today is toward green technology which focusing on asphalt pavement sustainability.

This creates an opportunity for the asphalt researcher to develop the sustainability indicator to reduce energy consumption and produce more recycled material. Such estimation tools could allow the industry and road agencies to recognize the impacts of different sustainable construction techniques, materials and methods, as well as the potential cost and resource savings [5]. The safety, efficiency and environmental friendly types of pavement need to be considered in order to produce a sustainable pavement. Sustainability of roadways can be improved by minimize the amount of energy consumed for their construction and efficiently use roadway materials to reduce waste [6, 7]. Consideration on the natural sources binder should be based on the factors and problems which related to the sustainability roadway construction. The benefits of using alternative binders could assist in saving the natural resources and also reducing energy consumption, while maintaining, and improving pavement

performance [8]. Most bituminous binders that are used for paving materials are obtained mainly from fossil fuels. With petroleum oil reserves becoming depleted and the need to establish a bio-based economy, it is important to produce binders from alternative sources, particularly from bio-renewable resources [9]. Using waste material for the binder will affect the environmental impacts of the material life cycle. Materials from bio fuel production and some of the biomass resources that may not be efficient for bio fuel production could be used to produce alternative binders [10]. Common alternative binders that has been used by other researchers are such as fossil fuel, bio-binder, soybean oil, palm oil, vegetable oil, engine oil residue, grape residues, swine waste, and pyrolysed materials [11]. Many advanced technologies have been acquired for the generation of bio-oil from biomass materials. Most of the effective technologies involve a pyrolysis process, which is a thermochemical process that heating organic materials in the absence of air and convert to solids, bio-oil and gases.

2.0 BIO-OIL PRODUCTION

Biomass can be changed to various strains of energy by numerous technical processes, depending on the raw material characteristics and the type of energy desired. As a result, a wide variety of conversion schemes has been developed. Chemical and structural analyses of the biomass samples are carried out according to the ASTM D1103-80 and ASTM D1104-56 standard test methods [12]. Among the various technologies, pyrolysis process is the simplest and oldest method in the production of charcoal, liquid, and gaseous products. Pyrolysis is a route for biomass utilization which has been widely applied for converting biomass liquid, gas and char. Pyrolysis liquid is referred by terms such as pyrolysis oil, bio-oil, bio-crude oil, bio-fuel oil, wood liquid, wood oil, liquid smoke, wood distillates, pyrolygneous tar, and pyrolygneous acid [13]. In general, bio-oil is produced from the pyrolysis process with temperature above 400°C, depends on the particle size of feedstock. Fast pyrolysis is one of the thermochemical process which converts the biomass into bio-oil (liquid), char (solid) and flue gas in the temperature range from 400°C to 600°C and in absence of oxygen [14]. In recent times, fast pyrolysis of biomass is one of the most promising technologies for converting biomass to liquid fuels [15]. The pyrolysis oils or bio-oil have water contents of typically 15–30 wt% of the oil mass, which cannot be removed by conventional methods like distillation [16]. Based on the findings of sugarcane bagasse (SB) and palm empty fruit bunch (EFB), SB the best operating conditions (temperature 560°C, gas residence time 77 s and particle size 0.5–0.85 mm) resulted in a bio-oil yield of 53.4 wt%, whereas in the case of EFB, the best operating conditions (temperature 540°C, gas residence time 31 s and particle size <0.5 mm) resulted in a bio-oil yield of 48.4 wt% [17]. Fast pyrolysis of rice husk has been performed in the range of 400–600°C in a pyrolysis process bench-scale plant equipped produced bio-oil yield is very high (70 wt.% at 450°C) due to the high capacity of mass and heat [18]. Bio-oil has higher energy density than biomass, can be readily stored and transported, and can be used either as a renewable liquid fuel or chemical production [19]. Maximum yield of bio-oil (47.3 wt%) can be obtained, working at the medium level for the operation temperature (500°C) and 2 L/min of N₂ flow rate at 60 min reaction time [20]. Temperature is the most important factor which will affect the yield product of bio-oil. Type of oils produced by several pyrolysis is dark brown liquid and has similar composition to biomass but it is not suitable for directly use for pavements material without any preheat and upgrading procedure as shown in Figure 1. The liquid fraction of the pyrolysis products

consists of two phases: an phase containing of organo-oxygen compounds of low molecular weight and a non-aqueous phase containing insoluble organics of high molecular weight [21]. Elemental Analyzer (EA) was used to determine CHNS (Carbon, Hydrogen, Nitrogen, Oxygen) in the bio-oil. Mostly the carbon content is higher then others in the chemical composition of bio-oil [22].



Figure 1 Bio-oil sample and standard bitumen

3.0 BIO-OIL PROPERTIES

Bio-oil is a complex mixture of several hundreds of organic compounds, mainly including acids, alcohols, aldehydes, esters, ketones, phenols, and lignin-derived oligomers [23]. Some of these compounds are directly related to the undesirable properties of bio-oil. Table 1 shows the properties of bio-oil, which obtained from different samples of biomass. The palm shell bio-oil has significantly higher moisture content from others sample. It can be seen that, higher moisture content will make it more difficult to obtain homogenous samples in the bio-oils. The water content of bio-oils contributes to their low energy density, lowers the flame temperature of the oils, leads to ignition difficulties, and, when preheating the oil, it can lead to premature evaporation of the oil and resultant injection difficulties [13]. Petroleum distillation oil has higher heating values (HHV) for the other samples and has been determined from experimental, but proximate values can be calculated by number of correlations. Higher heating values (HHV) measure the energy content which is important to characterize the fuels and others such as liquid, coal, gases and

biomass. The viscosities of biodiesels were much less than those of pure oils and their HHV's of approximately 42 MJ/kg were 10% less than those of petro diesel fuels [24]. HHV also has different effects on the pyrolysis products properties, including

biochar (element content, proximate analysis, specific surface area, heating value), bio-oil (water content, chemical composition), and non-condensable gas [25].

Table 1 Properties of pyrolysis bio-oils

Physical Properties	Black Alder Wood [12]	Palm Shell [26]	Petroleum distillate fuel oils ^b [27]	Values
Moisture content	15-30	30	<0.01	wt%
pH	2.5	3.27	-	-
Specific gravity	1.2	na	0.9477	-
Elemental Analysis				
C	54-58	47.6	87.03	wt%
H	5.5 – 7.0	8.1	10.85	wt%
O	35-40	43.7 ^a	-	wt%
N	0-0.2	0.6	0.43	wt%
S	-	-	0.05-0.08	wt%
Ash	0-0.2	<0.1	0.00	
HHV	16-19	17.9	43	MJ/kg

^aCalculated by different

^bInclude fuels that were spiked with Tert-Butyl Disulphide to gain wider study range of sulphur content

Higher water content in bio-oil can affect the performance of bio-oils and will lead to ignition and combustion problems. It is better to remove the water content from the pyrolysis samples before using the bio-oil directly in order to make it more concentrated. Normally sample heating is the most suitable method for the water to evaporate, but the appropriate temperature need to be identified. Another process is to use rotary evaporator apparatus in chemical laboratories for efficient removal of solvents from samples by evaporation[16]. Distillation bio-oil also more suitable for fuel oil use or as a source of chemicals compared to fast pyrolysis bio-oil [28]. The properties of the whole bio-oil are significantly altered when the bio-oil was heated at 80°C [29]. Carbon, hydrogen, nitrogen, oxygen and sulfur (CHNOS) are the basic elements in bio-oil chemical composition for quality, stability and upgrading.

4.0 ASPHALT BINDER

Asphalt or bitumen is widely used in road construction as a binder and has been identified as a sticky, black and highly viscous liquid or semi-solid form of petroleum. Due to traffic loads and environmental factors, asphalt properties will change during service life due to oxygen and UV radiation. Repeated loading will result in decreasing strength because of fatigueness. Water can influence the adhesion between asphalt and the aggregate and all these influences could lead to early failure [30]. Pavement asphalt binder in HMA will have a lower binder viscosity and workability but after compaction the mixture will gain higher viscosity which are needed for better cohesion and stability of the mixture. Most adhesives and binders, including binders for asphalt mixture production, are presently produced from petrochemicals through the refining of crude oil [31]. As asphalt is extracted from crude oil, which has variable composition according to its origin, the precise breakdown of hydrocarbon groups in bitumen is difficult to determine. However, elementary analysis of bitumen manufactured from a variety of crude sources show that most bitumens contain Carbon: 82-88%, Hydrogen: 8-11%, Sulphur: 0-6%, Oxygen: 0-1.5% and Nitrogen: 0-1% [32]. Asphalt binders also consist of four fractions including saturates, aromatics, resins and asphaltenes [33].

Regarding the aging performance, short term and long term aging tests are carried out using the Rolling Thin Film Oven Test (RTFOT) and the pressure aging vessel (PAV) respectively, following the standard practice outlined by American Association of State Highway and Transportation Officials (AASHTO) [34]. The aging properties of asphalt binders are normally characterized by measuring physical and rheological properties (e.g. softening point, penetration, viscosity and complex modulus) before and after artificial aging in the laboratory [35, 36]. Modified asphalt is a solution of altering and improving the properties of the bitumen to enhance the long term performance of pavements [37]. Bio-oil is blended with the base binder as an additives at different percentage values of weight binder to produce bio modified binder by using mixer and suitable rotation speed and time. Suitable percentages are used for bio-oil to determine if the liquid can act as partial substitute of asphalt binder in order to reduce the amount of asphalt required. Normally asphalt base binder needs to be heated at temperature of 145°C to 185°C depending on the grade of asphalt [38]. To do so, both material need to be heated and blended together before performance tests and it has shown that the blending caused a very intense volumetric expansion initially and the incurred air bubbles disappeared after some rest time [39]. For instance, waste edible vegetable oil is blended using the propeller mixer at a constant speed of 1200 rpm for 15 min at 130°C [33]. Similarly the control asphalt binder and the bio-oil modifier from waste wood mixed for 20 min at 130 °C using a high shear mixer shearing rate of 5000 rounds per minute (RPM) [40]. Dynamic Shear Rheometer (DSR) according to ASTM D7175 and a master curve at 25°C is automatically created for each sample for rheological properties of the binder performance [41]. DSR test are used to understand the different characteristic aging behavior of bio-oil modified asphalt by determine the high temperature rheological properties which is related to mixability and rutting resistance for unaged sample [42].

Hence modified bio-oil should also response to rheological and mechanical tests which are performed to characterize for different grade of the asphalt. The rheological properties requirement for asphalt during mixing and compaction are summarized in Table 2.

Table 2 Engineering requirement for bitumen [43]

Behavior during :	Condition		Significant property of the bitumen in the mix
	Temperature (°C)	Time of Loading (s)	
Application			
Mixing	High (100°C)	-	Viscosity approximately 0.2 Pas
Laying	High	-	Viscosity
Compaction	High	-	Viscosity minimum 5 Pas Maximum 30 Pas
In service			
Permanent deformation	High temperature (30-60°C)	road	Long $>10^{-2}$
Fatting up	High temperature (30-60°C)	road	Long $>10^{-2}$
Cracking			
-Traffic stresses	Low Temperature	road	Short (10^{-2})
-Thermal stresses	Low Temperature	road	Long
-Fretting	Low Temperature	road	Short $>10^{-2}$
			Maximum bitumen stiffness

4.1 Performance Bio-oil Modified Asphalt Mixtures

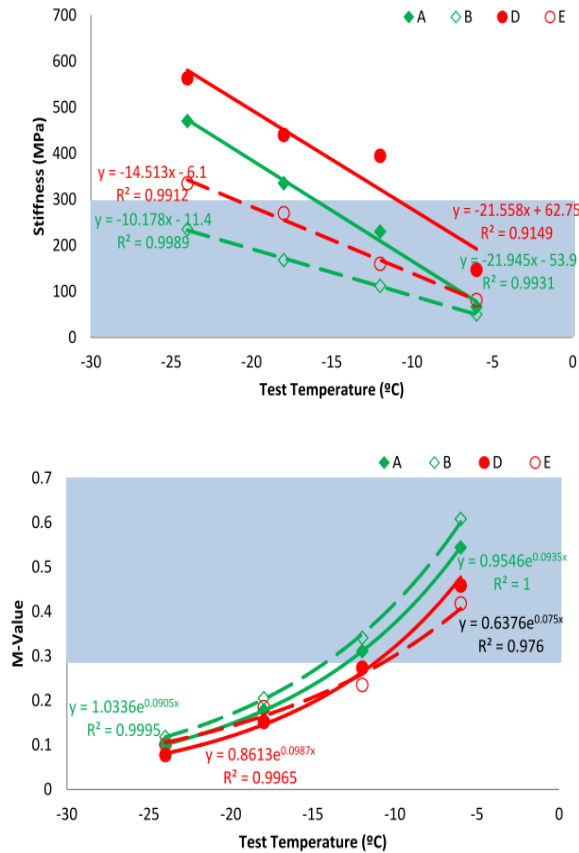
In addition of the environmental benefits, the production of bio binder from biomass is the better idea and will reduce the demand of the bitumen. Bio-binder is a renewable sources of fuel made from biomass resources [44]. In 2011, Malaysian Biomass Industries Consideration (MBIC) developed the biomass industry to commercialize, marketing and utilizing the applications of biomass product for sustainable growth of biomass industry. The biomass industry represents several different industries brought together by the utilization of renewable organic matters including timber waste, oil palm waste, rice husk, coconut trunk fibers, municipal waste, sugar cane waste, etc. Bio based binders have mostly captured certain place markets (microsurgery, paper coatings, and pavement industry), but many end-users in other industrial sectors have now begun to show a real shift in their attitude and approach towards bio based binders [45]. An alternative approach for decreasing the demand and dependency for crude petroleum/bitumen binders is the use of bio-binders in three different ways: a direct alternative binder (100% replacement), a bitumen extender (25% to 75% replacement), or a bitumen modifier (<10% replacement) [46]. The bio-oil from pyrolysis process has been blended with the asphalt as modified asphalt binder. Increased demand for asphalt, along with the need for improved asphalt materials/pavement performance, creates the opportunity for bio-renewable asphalt modifiers and/or asphalt substitutes [47]. Determination of optimum percentage of bio-oil is very important to establish the rheological properties and pavement performance. Modification of asphalt mixtures is expected to improve the material strength, fatigue resistance and mechanical properties [48]

The blending for the 80-200 mesh crumb rubber and petroleum based binder (PG 64-22) was completed at three percentages of crumb rubber (5%, 10%, and 15%) with one percentage of bio- binder (5%) by the weight of the petroleum based binder [10]. Modified asphalt is produced from waste cooking oil after undergoing the thermochemical process which involves the polymerization process at elevated temperature and known as bio asphalt [4]. It has been proved that the rheological properties of the asphalt binder affect the pavement performance. For this reason, bio binder has gained much more considerable benefits of blending the bio-oil as asphalt binder

and improve the rheological properties and pavement performance.

The rheological properties of switch grass bio-oils are similar and comparable to bitumen binders and represent a viable renewable alternative to petroleum derived asphalt binders [46]. It is also found that bio-binder asphalt modification improved the low temperature fracture performance of the mixtures when compared to conventional mixtures of similar performance grade [44]. The bio-oil (red oak mood) can successfully react with crumb rubber at 125°C, which is a substantially lower temperature than that used in normal asphalt binders, typically around 185°C [49]. Determination of the low temperature for asphalt binder performance grade (PG) is conducted using Bending Beam Rheometer (BBR) on long term aged Asphalt samples for the physical properties. The cracking temperature, T_{cr} , is usually calculated from BBR test results using the AASHTO T 313 procedure, as the higher value between the temperature in which the stiffness at a loading time of 60 s is 300MPa and the temperature in which the m -value at a loading time of 60 s is 0.3 [50]. Figure 2 shows the result from BBR testing of bio-oil blend with two sources of rubber-mechanical-shredding rubber and cryogenic ambient rubber as main material.

From the result presented in Figure 2, the performance of bio-oils with modification of rubber is very good at -10°C which corresponds to a field temperature of -20°C. It also shows that the bio-oil consist 10% cryogenic rubber has lower temperature grade based on the regression line. Based on the m - value findings, bio-oils modification at low temperature below the test temperature of -10°C shows an improvement. The best performance m -values materials to this parameter are bio-oils produced from cryogenic rubber. The interaction of the modification of to the mechanical properties of asphalt mixtures is important to fatigue, cracking, rut depth and others. Addition wastes wood of bio-oils significantly improves the asphalt mixture fatigue performance where it has no significant effect on the rutting performance and dynamic modulus, but slightly impacted the tensile strength [40]. Bio-oils derived from waste wood are blended with the asphalt petroleum PG58-28 as asphalt mixtures and produced Bio-oil Modified (BOM), the Original Bio-oil (OB) and Polymer Modified Bitumen (PMB).



*A = 90% bio-oil and 10% cryo rubber, B=85% bio-oil and 15% cryo rubber, D= 90% bio-oil and 10% amb rubber, E = 90% bio-oil and 15% amb rubber

Figure 2 The BBR stiffness and m-values with the test temperature [49]

Figure 3 shows the dynamic modulus (E^*) master curve plot for control asphalt mixture are tested at different temperatures. Original Bio-oil (OB) of Bio-oil Modified (BOM) asphalt mixtures indicate slightly higher E^* than the control asphalt mixture when increased the additive of bio-oil. From the both master curves, it is found that addition 10% of Polymer Modified Bitumen (PMB) shows the curves are plotted slightly nearest control asphalt mixtures compared 5% of Original Bio-oil (OB). It can be seen that the addition of Polymer Modified Bitumen (PMB) asphalt mixtures increase the stiffness of asphalt mixtures more significantly at relatively higher temperatures. Asphalt bitumen usually composes over 90% of the PMB by weight, which could introduce overriding influences on the final properties of the PMB [51]. Good quality asphalt base can influence the effects of polymer modification, while poor quality one may make the unsatisfied results.

5.0 CONCLUSION

This review has focused on the study of pyrolysis techniques to produce high grade bio-oil for asphalt mixtures additives and modifier. The studies in the literature have been used to support the analysis and discussion in this paper. Many researchers have recognized that the bio-oil can significantly improve the quantity and quality of asphalt mixture with modification of

Polymer Modified Bitumen (PMB). Strategic management decomposing biomass and utilizing the biomass, which encourage the use of bio-oil from biomass as renewable sources to the asphalt mixtures for pavement. Application of sustainability concepts to the pavement relationship of energy and material is proposed to be incorporated into pavement engineering and management. Therefore, relationship between rheological binder properties and mixture performance will provide the sustainable practice of modified version in the generic classification of asphalt additive and modifiers.

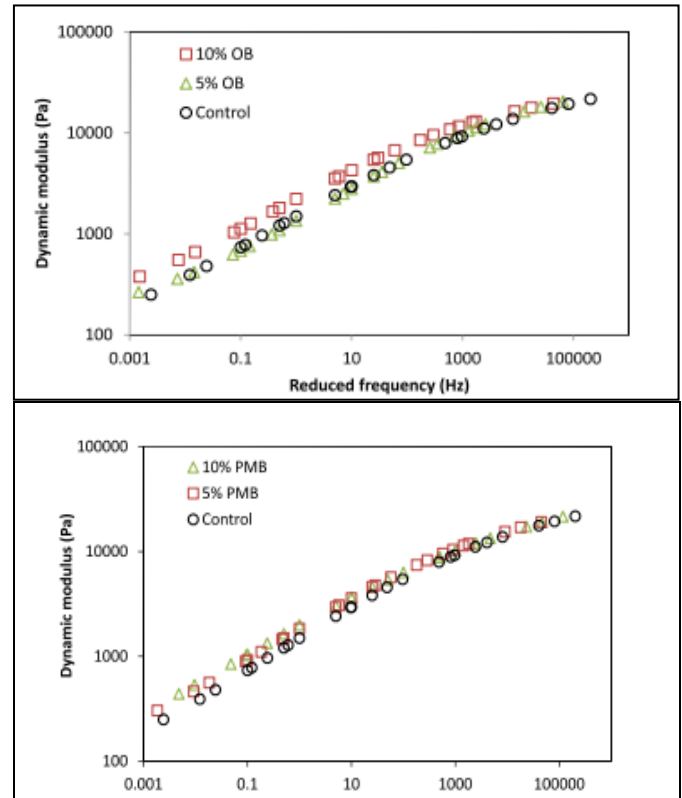


Figure 3 Mechanical performance of asphalt mixtures using modified of bio-oil (wastes wood) [40]

Acknowledgement

The authors would like to extend their gratitude to Universiti Teknologi Malaysia Research Grants (GUP Tier 1 Vote 06H58), Jabatan Pengajian Politeknik(JPP) and Kementerian Pelajaran Malaysia(KPM) for the financial support in this research project.

References

- [1] S. Dunn and J. Holloway. 2012. *The Pricing of Crude Oil*. 65–74.
- [2] P. Taylor, E. H. Fini, I. L. Al-qadi, Z. You, and B. Zada. 2012. *International Journal of Pavement Engineering*. Partial Replacement of Asphalt Binder With Bio-binder: Characterisation and Modification. 37–41.
- [3] S. A. Yero And M. R. Hainin. 2012. Viscosity Characteristics of Modified Bitumen. *Arpn J. Sci. Technol.* 2(5): 500–503.
- [4] H. Wen, M. Asce, S. Bhusal, and B. Wen. 2013. Laboratory Evaluation Of Waste Cooking Oil-Based Bioasphalt As An Alternative Binder For Hot Mix Asphalt. 25(10): 1432–1437.
- [5] T. D. Miller. 2009. Sustainable Asphalt Pavements: Technologies, Knowledge Gaps and Opportunities.

- [6] M. R. Hainin, R. P. Jaya, N. A. A. Bakar, D. S. Jayanti, And N. I. M. Yusoff. 2014. Influence of Palm Oil of Fuel Ash on Bitumen to Improve Aging Resistance. *Journal of Engineering Research*. 1(2): 1–13.
- [7] R. Zakaria, F. K. Seng, R. M. Zin, M. R. Hainin, O. C. Puan, N. Derin, F. Ainee, N. Hamzah, S. O. Balubaid, A. N. Mazlan, M. A. Ismail, S. Yazid, R. Rafidah, R. Mohd, And F. Moayed. 2013. Efficiency Criteria For Green Highways In Malaysia. *J. Teknol. Energy*. 3: 91–95.
- [8] S. C. Huang, D. Salomon, And J. Haddock. 2012. Alternative Binders For Sustainable Asphalt Pavements. In *Laboratory Of Waste Cooking Oil-Based As Sustainable Binder For Hot-Mix Asphalt*.
- [9] J. Peralta, C. R. Williams, Marjorie Rover, and Hugo M.R.D. Silva, 2012. Development Of Rubber-Modified Fractionated Bio-Oil For Use As Noncrude Petroleum Binder In Flexible Pavements. *Transp. Res. Circ. Altern. Bind. No. Alternative Binders For Sustainable Asphalt Pavements*.
- [10] E. H. Fini, M. Asce, D. J. Oldham, and T. Abu-lebdeh. 2013. Synthesis and Characterization of Biomodified Rubber Asphalt: Sustainable Waste Management Solution for Scrap Tire and Swine Manure. 3(December): 1454–1461.
- [11] P. Taylor, S. Pouget, and F. Loup. 2013. Road Materials and Pavement Design Thermo-mechanical behaviour of mixtures containing bio-binders. November: 37–41.
- [12] P. Taylor and A. Demirbas. 2009. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects Fuel Properties of Pyrolysis Oils from Biomass. January 2014: 37–41.
- [13] M. Balat, M. Balat, E. Kirtay, and H. Balat. 2009. Main Routes for the Thermo-Conversion of Biomass Into Fuels and Chemicals. Part 1: Pyrolysis Systems. *Energy Convers. Manag.* 50(12): 3147–3157.
- [14] A. A. Salema and F. N. Ani. 2010. Microwave Pyrolysis of Oil Palm Fibres. *J. Mek. Univ. Teknol. Malaysia*. 30: 77–86.
- [15] Q. Lu, W.-Z. Li, and X.-F. Zhu. 2009. Overview of Fuel Properties of Biomass Fast Pyrolysis Oils. *Energy Conversion and Management*. 50(5): 1376–1383.
- [16] P. Taylor, S. Kele, K. Kaygusuz, and M. Akgün. 2014. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects Pyrolysis of Woody Biomass for Sustainable Bio-oil. July: 37–41.
- [17] S. Ciuta, F. Patuzzi, M. Baratieri, and M. J. Castaldi. 2014. Journal of Analytical and Applied Pyrolysis Biomass Energy Behavior Study During Pyrolysis Process By Intraparticle Gas Sampling. *J. Anal. Appl. Pyrolysis*. 108: 316–322.
- [18] J. Alvarez, G. Lopez, M. Amutio, J. Bilbao, and M. Olazar. 2014. Bio-oil Production from Rice Husk Fast Pyrolysis in a Conical Spouted Bed Reactor. *FUEL*. 128:162–169.
- [19] P. Taylor and M. Balat. 2011. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects An Overview of the Properties and Applications of Biomass Pyrolysis Oils An Overview of the Properties and Applications of Biomass Pyrolysis Oils. July 2014: 37–41.
- [20] F. Abnisa, W. M. A. W. Daud, W. N. W. Husin, and J. N. Sahu. 2011. Utilization Possibilities of Palm Shell as a Source of Biomass Energy in Malaysia By Producing Bio-Oil in Pyrolysis Process. *Biomass and Bioenergy*. 35(5): 1863–1872.
- [21] A. Demirbas. 2009. Pyrolysis of Biomass for Fuels and Chemicals. *Energy Sources, Part A Recover. Util. Environ. Eff.* 31(12): 1028–1037.
- [22] A. Shah, M. J. Darr, D. Dalluge, D. Medic, K. Webster, and R. C. Brown. 2012. Bioresource Technology Physicochemical Properties Of Bio-Oil and Biochar Produced by Fast Pyrolysis of Stored Single-Pass Corn Stover and Cobs. *Bioresour. Technol.* 125: 348–352.
- [23] S. Xiu and A. Shahbazi. 2012. Bio-oil Production and Upgrading Research: A Review. *Renewable and Sustainable Energy Reviews*. 16(7): 4406–4414.
- [24] K. Sivaramakrishnan. 2011. Determination Of Higher Heating Value Of Biodiesels. 3(11): 7981–7987.
- [25] D. Chen, J. Zhou, and Q. Zhang. 2014. Bioresource Technology Effects of Heating Rate on Slow Pyrolysis Behavior, Kinetic Parameters and Products Properties of Moso Bamboo. *Bioresour. Technol.* 169: 313–319.
- [26] S. Kim, S. Jung, and J. Kim. 2010. Bioresource Technology Fast Pyrolysis of Palm Kernel Shells: Influence of Operation Parameters on the Bio-oil Yield and the Yield of Phenol and Phenolic Compounds. *Bioresour. Technol.* 101(23): 9294–9300.
- [27] S. W. Lee, T. Herage, I. He, and B. Young. 2008. Particulate Characteristics Data for the Management Of PM_{2.5} Emissions From Stationary Combustion Sources. *Powder Technol.* 180(1–2): 145–150.
- [28] J.-L. Zheng and Q. Wei. 2011. Improving the Quality of Fast Pyrolysis Bio-oil by Reduced Pressure Distillation. *Biomass and Bioenergy*. 35(5): 1804–1810.
- [29] A. Chaala, T. Ba, M. Garcia-Perez, C. Roy, and D. Rodrigue. 2004. Colloidal Properties of Bio-oils Obtained by Vacuum Pyrolysis of Softwood Bark: Aging and Thermal Stability. *Energy & Fuels*. 18(5): 1535–1542.
- [30] S. Wu, J. Wang, and L. Jiasheng. 2010. Preparation and Fatigue Property of Nanoclay Modified Asphalt Binder. *2010 Int. Conf. Mech. Autom. Control Eng.* 1595–1598.
- [31] G. D. Airey, M. H. Mohammed, and C. Fichter. 2008. Rheological Characteristics of Synthetic Road Binders. *Fuel*. 87: 10–11, 1763–1775.
- [32] M. Rahman. 2004. Characterisation of Dry Process Crumb Rubber Modified Asphalt Mixtures. The University of Nottingham.
- [33] M. Chen, B. Leng, S. Wu, and Y. Sang. 2014. Physical, Chemical And Rheological Properties Of Waste Edible Vegetable Oil Rejuvenated Asphalt Binders. *Constr. Build. Mater.* 66: 286–298.
- [34] M. K. Idham, M. R. Hainin, H. Yaacob, M. N. M. Warid, and M. E. Abdullah. 2013. Effect Of Aging On Resilient Modulus Of Hot Mix Asphalt Mixtures. *Adv. Mater. Res.* 723: 291–297.
- [35] P. Cong, J. Wang, K. Li, and S. Chen. 2012. Physical and Rheological Properties of Asphalt Binders Containing Various Antiaging Agents. *Fuel*. 97: 678–684.
- [36] N. I. Md. Yusoff, G. D. Airey and M. R. Hainin. 2010. Predictability of Complex Modulus Using Rheological Models. *Asian Journal of Scientific Research*. 3(1): 18–30.
- [37] M. R. Hainin, M. N. M. Warid, R. Izzul, M. K. Ruzaini, and M. I. M. Y. 2014. Investigations of Rubber Dipping By-Product on Bitumen Properties. 911: 449–453.
- [38] H. Yaacob, M. R. Hainin, M. Maniruzzaman, M. N. M. Warid, F.-L. Chang, and C. R. Ismail. 2013. Bitumen Emulsion In Malaysia-A Conspectus. *J. Teknol.* 3: 97–104.
- [39] H. Wang and Kristen Derewecki. 2013. Rheological Properties of Asphalt Binder Partially Substituted With Wood Lignin. 977–986.
- [40] X. Yang, Z. You, Q. Dai, and J. Mills-Beale. 2014. Mechanical Performance of Asphalt Mixtures Modified By Bio-Oils Derived From Waste Wood Resources. *Constr. Build. Mater.* 51: 424–431.
- [41] S. Zhao, B. Huang, X. P. Ye, X. Shu, And X. Jia. 2014. Utilizing Bio-Char as a Bio-modifier for Asphalt Cement: A Sustainable Application Of Bio-fuel By-Product. *Fuel*. 133: 52–62.
- [42] N. H. M. Kamaruddin, M. R. Hainin, N. A. Hassan, and M. E. Abdullah. 2014. Rutting Evaluation of Aged Binder Containing Waste Engine Oil. *Adv. Mater. Res.* 911: 405–409.
- [43] Shell Bitumen. 2003. *The Shell Bitumen Handbook*. Fifth Edit. London, Uk, P. 190.
- [44] L. N. Mohammad, M. Elseifi, S. B. Cooper, and P. Naidoo. 2013. Laboratory Evaluation of Asphalt Mixtures Containing Bio-binder Technologies. 128–152.
- [45] S. H. Imam, C. Bilbao-Sainz, B.-S. Chiou, G. M. Glenn, and W. J. Orts. 2013. Biobased Adhesives, Gums, Emulsions, And Binders: Current Trends And Future Prospects. *J. Adhes. Sci. Technol.* 27(18–19): 1972–1997.
- [46] M. A. Raouf And C. R. Williams. 2010. General Rheological Properties of Fractionated Switchgrass Bio-Oil as a Pavement Material. *Road Materials And Pavement Design*. 11(Sup1): 325–353.
- [47] J. Peralta, M. Raouf, S. Tang, and R. Williams. 2012. Bio-Renewable Asphalt Modifiers and Asphalt Substitutes. *Sustain. Bioenergy*. 89–115.
- [48] O. S. Abiola, W. K. Kupolati, E. R. Sadiku, and J. M. Ndambuki. 2014. Utilisation Of Natural Fibre As Modifier In Bituminous Mixes: A Review. *Constr. Build. Mater.* 54: 305–312.
- [49] J. Peralta, C. R. Williams, Marjorie Rover, and Hugo M. R. D. Silva. 2012. Alternative Binders for Sustainable Asphalt Pavements. In *Development Of Rubber-Modified Fractionated Bio-Oil For Use As Noncrude Petroleum Binder In Flexible Pavements*. 23–36.
- [50] P. Taylor, E. H. Fini, I. L. Al-Qadi, Z. You, And B. Zada. 2012. *International Journal Of Pavement Engineering Partial Replacement Of Asphalt Binder With Bio-Binder: Characterisation And Modification*. 37–41.
- [51] J. Zhu, B. Birgisson, And N. Kringos. 2014. Polymer Modification Of Bitumen: Advances And Challenges. *Eur. Polym. J.* 54: 18–38.