

Optimization of Bio Asphalt Derived from Pyrolysis Bio Oil for Bitumen Modification

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Abstract. Due to inadequate crude oil supply and a rising demand for petroleum asphalt in road construction, the asphalt sector faces a continuing shortage. Continuous research was conducted on renewable materials such as bio-oils derived via pyrolysis from local palm oil industries. Bio-oil is currently a viable option due to its renewability, environmental friendliness, and variety of sources. Despite numerous studies indicating that bio-oils enhance the properties of bitumen, the research on the effects of PKS bio-oil on bitumen properties is minimal and needed further investigations. The application of 2,4-diphenylmethane diisocyanate (MDI) in this study is established to enhance the properties of bio-oil modified bitumen. The objectives of this study are to analyse the relationship between the percentage and ratio of PKS bio-oil and 2,4-diphenylmethane diisocyanate (MDI) of the modified bitumen, its physical and chemical effects and the optimization of bio-asphalt mixture after the 2,4-diphenylmethane diisocyanate (MDI) has been blended with PKS bio-oil and bitumen. PKS bio-oil and MDI were applied into the bitumen as additive and replacement of bitumen at 3%, 5% and 7% with two different ratios; 1.0:0.6 and 1.0:1.0. The functional groups of the bitumen are identified using Fourier Transform Infrared (FTIR) analysis. The result generated from FTIR analysis showed that the modified bitumen samples were slightly different when compared to the conventional bitumen regarding the functional group. Response surface methodology (RSM) was implemented to determine the statistical analysis and optimum amount of PKS bio-oil and MDI content in the bitumen, through central composite design.

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1 Introduction

With a low supply of crude oil and an increasing demand for petroleum asphalt in pavement construction, the asphalt industry experiences a persistent shortage. Engineers, experts and researches have been searching for methods to limit the consumption of asphalt made from virgin petroleum. Utilizing other optional materials is one of the most successful and environmentally friendly strategies for addressing this issue [1, 2, 3, 4]. Nowadays, experts have determined that bio-oil is a viable choice due to its diversity of sources, environmental friendliness and renewability [5, 6]. Bio-oils are a form of renewable material produced from biomass [6].

The term "biomass" refers to waste products derived from plants or animals that are not fit for use as either food or feed. Materials include animal and plant corpses as well as human waste from sewage facilities. Examples of corps include palm kernels, rice stalks, food waste such as corn cobs, animal excretions such as swine manure, and animal and plant corpses [7]. Another study stated that biomass can be utilized in a wide variety of industrial processes, including the creation of energy, the manufacture of raw materials for chemical manufacturing, and the development of a new way for cleaner production [8]. The term "bioenergy" refers to the potential energy that may be extracted from biomass. Biomass contains a variety of chemicals, including light ones like diesel, bio-diesel, solvent, hydrogen, and bio-gasoline, as well as heavy ones, most notably bio-oil. Bio-oils are a form of renewable material produced from biomass [6].

Bio-oil is created by recycling various sources and has lower-molecular-weight components that resemble small portions of the virgin asphalt binder applied to road construction roadways. Bio-oil can be used as a replacement material for the modification of asphalt [9]. It has been proposed that conventional asphalt binders could benefit from the addition of bio-oils, which can be produced from palm oil waste. Particularly, bio-oils that are generated from palm oil wastes are recommended as a potential additive to conventional asphalt binder [10, 11].

2 Methodology

2.1 General

In order to achieve the goals of this study, each step of the process that involve in it was explained in great detail. The methodology that were used in this study were carried out in a methodical manner, starting with the gathering of materials such as PKS bio-oil, MDI and bitumen. This is followed by laboratory work related to the characteristics of bitumen, which included the preparation of bio-oil modified bitumen and the testing of bitumen. The testing procedures for bitumen are broken down into two categories: the physical test and the chemical test. Penetrating test, softening point test, and ductility test are included in the physical test. The Fourier Transform Infrared (FTIR) test is used for the chemical analysis of the modified bitumen samples. For the purpose of modelling and analysing the mixing parameters of PKS bio oil, MDI, and bitumen, statistical analysis and optimization of bio-asphalt are performed using Response Surface Methodology (RSM). Then the conclusive interpretation of the data is presented. Figure 1 presents a flowchart of the research methodology.

Prior to the addition of PKS bio-oil to the sample, 300g of bitumen will be employed in this investigation. The percentages of bio-oil are consistent with the percentages used by Al-Omari *et al.* and Gurer *et al.* [12, 13], which both employ 2% increment percentages. Both Al-Omari *et al.* and Gurer *et al.* [12], [13] up to 8% and 9% of bio-oil. In this study, the PKS bio-oil to MDI ratio was 100:60 (parts by weight) as implemented in a study conducted by

Khairuddin *et al.* [14]. Samples with a different ratio of PKS bio-oil to MDI of 100:100 (parts by weight) is also applied in this study to compare the findings of different ratios and another sample with no addition of bio-oil and MDI. The procedure of blending bio-oil with bitumen is undertaken based on the availability and capability of the procedure of blending bio-oil with bitumen is undertaken based on the availability and capability of the laboratory's equipment.

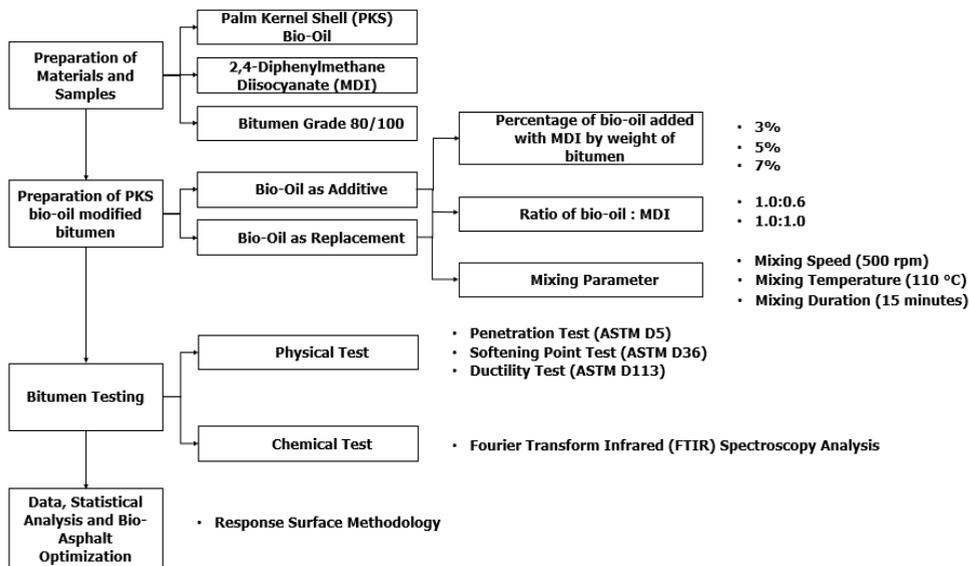


Fig. 1. Flow chart of research methodology.

2.2 Materials and Samples Preparation

PKS bio-oil and control bitumen with a penetration grade of 80/100 are the materials that were used for the laboratory work associated with this study. Due to the heavy traffic load and hot climate in Malaysia, the conventional bitumen grade most frequently used is 80/100 penetration grade. This particular grade of bitumen is typically applied in the production of hot mix asphalt, both for roadway bases and wearing courses [15]. The PKS bio-oil implemented in this study was originally acquired from the local palm oil industry in Lahad Datu, Sabah. The PKS bio-oil is specifically acquired from Lahad Datu due to its wide availability of palm kernel shell and the enhanced facility of the manufacturer to produce PKS bio-oil from pyrolysis process.

2.3 Experimental Procedure

Figure 2, Figure 3 and Figure 4 show the PKS bio-oil, MDI and bitumen which are the materials used in this study. 300g of bitumen will be employed in this investigation. The percentages of PKS bio- oil and MDI applied are 3%, 5% and 7% by weight of bitumen. PKS bio-oil to MDI ratio was 100:60 (parts by weight). Samples with ratio of PKS bio-oil to MDI of 100:100 (parts by weight) is also applied in this study to compare the findings of different content and another sample with no addition of bio-oil and MDI. Conventional physical tests; penetration test (ASTM D5); softening point test (ASTM D36); ductility test (ASTM D113) for bitumen is conducted to analyse the physical properties of the modified bitumen. Chemical test using Fourier Transform Infrared (FTIR) is also conducted to identify the

chemical composition and the functional groups of the modified bitumen. For easier identification sample designation was used. For example, CB is referred as 'control bitumen', A as 'additive' and R as 'replacement'. The first number denotes the percentages of additive or replacement.



Fig. 2. PKS bio-oil.

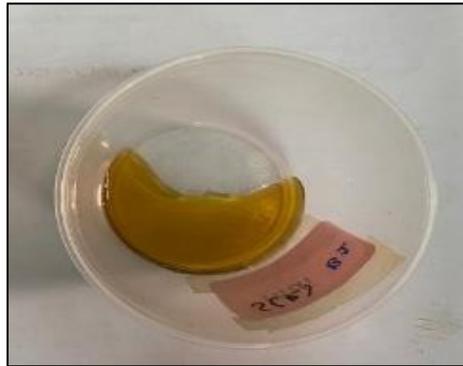


Fig. 3. 2,4-diphenylmethane diisocyanate (MDI).



Fig. 4. Bitumen Grade 80/100.

3 Results and Discussion

3.1 Penetration Test

The finding of penetration test shows that in increasing percentage of bio-oil and MDI result in higher value of penetration for both addition and replacement. The modified bitumen with bio-oil to MDI ratio of 1.0:1.0 shows better performance than the samples with 1.0:1.0 bio-oil to MDI content. The penetration values Samples 3A2, 3R1 and 3R2 were reduced to be <80 dmm with the addition and replacement of 3% bio-oil and MDI. Both 3% addition and replacement show the best result in penetration compared to other samples of higher percentage. The increasing penetration depth of the samples implies that the PKS bio-oil has softened the bitumen since 5% of bio-oil modification showed 122 dmm and 106 dmm (additive and replacement, respectively) penetration which is not within the range of the control bitumen grade. However, for samples 5A2 and 5R2, the penetration values are still within the standard. The penetration of PKS bio-oil modified bitumen with MDI is shown in Table 1.

Table 1: The penetration of the PKS bio-oil modified bitumen.

Sample Code	Bio-Oil and MDI (%)	Ratio Bio-Oil:MDI (g)	Penetration (dmm)
CB	-	-	83
3A1	3	1.0:0.6	85
3A2	3	1.0:1.0	66
5A1	5	1.0:0.6	122
5A2	5	1.0:1.0	89
7A1	7	1.0:0.6	137
7A2	7	1.0:1.0	106
3R1	3	1.0:0.6	74
3R2	3	1.0:1.0	66
5R1	5	1.0:0.6	106
5R2	5	1.0:1.0	86
7R1	7	1.0:0.6	128
7R2	7	1.0:1.0	112

3.2 Softening Point Test

In terms of temperature susceptibility, the control bitumen is compared to the bio-oil and MDI modified bitumen at 48.3 °C, the temperature at which the virgin bitumen becomes susceptible to higher temperature. It can be seen from Figure 2 that higher content of bio-oil and MDI decreased softening point of the modified bitumen. Based on Table 2, The control bitumen has the softening point of 48.3 °C, whereas it becomes, 46.0 °C, 43.5 °C to 43.0 °C and 46.5 °C, 45.5°C to 44.8 °C with the addition of 1.0:0.6 and 1.0:1.0 bio-oil to MDI, respectively. It is also notable that the replacement of 1.0:0.6 and 1.0:1.0 modifier has reduced the softening point from 48.3 °C to 45.8 °C, 43.5 °C, 42.5 °C and 48.0 °C, 46.0 °C, 43.8 °C, respectively. The standard specification by Jabatan Kerja Raya (JKR) for softening point of PG 80/100 ranges from 45-52 °C. Thus, it clearly shows that 7% additive and replacement of bio-oil failed to meet the standard. As for 5% additive and replacement, only the bio-oil and MDI content with ratio of 1.0:0.6 failed to satisfy the specification by JKR. In this study, the lowest softening point is recorded from a 7% replacement which is 42.5 °C.

Table 2: The softening point of the PKS bio-oil modified bitumen.

Sample Code	Bio-Oil and MDI (%)	Ratio Bio-Oil:MDI (g)	Penetration (dmm)
CB	-	-	48.3
3A1	3	1.0:0.6	46.0
3A2	3	1.0:1.0	46.5
5A1	5	1.0:0.6	43.5
5A2	5	1.0:1.0	45.5
7A1	7	1.0:0.6	43.0
7A2	7	1.0:1.0	44.8
3R1	3	1.0:0.6	45.8
3R2	3	1.0:1.0	48.0
5R1	5	1.0:0.6	43.5
5R2	5	1.0:1.0	46.0
7R1	7	1.0:0.6	42.5
7R2	7	1.0:1.0	43.8

All unmodified and modified bitumen samples have been subjected to a penetration test and softening point test to determine their penetration and softening point, respectively. These physical properties are correlated in terms of the bitumen's hardness and temperature susceptibility. Figure 5 shows the results of correlation of penetration and softening point. The result shows the higher the penetration value, the lower the softening point. Accordance to a study conducted by Abdul [16], it is reported that the data for the softening point must be consistent with the data for penetration. When bitumen has lower penetration value, its softening point must be greater. In contrary, when bitumen has higher penetration value, it results in lower value of softening point.

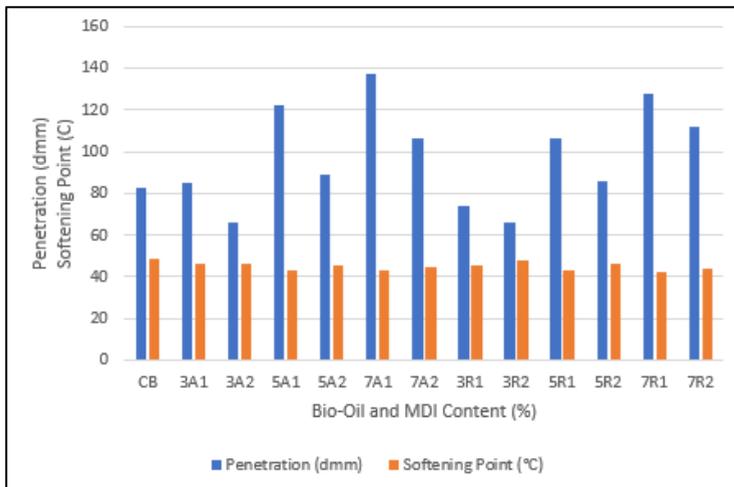


Fig. 5. The penetration value and softening point of the original and PKS bio-oil and MDI modified bitumen.

3.3 Ductility Test

Based on Table 3, the ductility values decreased as the PKS bio-oil and MDI addition and replacement increased to the bitumen. However, the replacement of bitumen shows a slightly higher ductility value compared to the addition of PKS bio-oil and MDI into the original bitumen. It also shows that the ratio 1.0:0.6 of bio-oil to MDI resulted in higher value of ductility compared to the ratio of 1.0:1.0 of bio-oil to MDI content. The ductility value is less than the JKR's standard which is minimum of 100 cm. Therefore, the incorporation of 3%, 5% and 7% with 1.0:1.0 and 1.0:0.6 ratio of PKS bio-oil and MDI into bitumen did not fulfil the requirement and is not suitable for pavement usage. In general, bitumen with 80/100 penetration grade has the value of ductility more than 100 cm. As the PKS bio-oil modified bitumen get harder and stiffer, it is predicted that there will be reduction of the ductility values. Addition and replacement of bio-oil and MDI to viscous bitumen tends to lessen the ductile characteristic of the material. This statement is supported by a study of addition of polyethylene into bitumen made by Chen *et al.* [17] which stated, as the polyethylene content of the binder increased, the ductility values decreased and as the modified bitumen becomes more hard and stiff, a decrease in ductility is expected and inevitable.

Table 3: The penetration of the PKS bio-oil modified bitumen.

Sample Code	Bio-Oil and MDI (%)	Ratio Bio-Oil:MDI (g)	Penetration (dmm)	Remarks
CB	-	-	149.2	Passed the minimum standard (>100 cm)
3A1	3	1.0:0.6	47.6	Did not pass the minimum standard (<100 cm)
3A2	3	1.0:1.0	39.6	
5A1	5	1.0:0.6	51.7	
5A2	5	1.0:1.0	21.3	
7A1	7	1.0:0.6	20.7	
7A2	7	1.0:1.0	18.8	
3R1	3	1.0:0.6	68.5	
3R2	3	1.0:1.0	53.3	
5R1	5	1.0:0.6	34.7	
5R2	5	1.0:1.0	20.8	
7R1	7	1.0:0.6	28.4	
7R2	7	1.0:1.0	25.3	

3.4 Fourier Transform Infrared Spectroscopy (FTIR) Test

Figure 6 depicts the transmittance of the infrared (IR) spectrum obtained for the modified bitumen samples; 3% to 7% with ratio 1.0:1.0 and compared to the original bitumen sample. For the functional groups to be examined from this study, the wavenumbers are taken from 400 cm^{-1} to 4000 cm^{-1} . All unmodified and modified bitumen samples revealed clear peaks at 2920 cm^{-1} , 2852 cm^{-1} , 1456 cm^{-1} and 1376 cm^{-1} which corresponded with ACH_3 and ACH_2 . The 2852 cm^{-1} and 2920 cm^{-1} high intensity of CH_2 bands were related with saturated hydrocarbons; the 1600 cm^{-1} medium intensity. The next crucial absorption peaks are C-O bond that attached with C=C that is known as C=O Stretching (Carbonyl group) at 1700 cm^{-1} and C=C (aromatic) bond at 1600 cm^{-1} which indicate the stretching vibration of the aromatic hydroxyl. 1511 cm^{-1} represents the C=C stretching which indicates the presence the

aromatic ring. This result is aligned with the study conducted by Alamawi *et al.* [18] which stated, through the MDI reaction, there is the presence of C=C aromatic ring at 1500–1700 cm^{-1} . The wavenumber of the stretching vibration of the sulfoxide bond, S=O, is 1030 cm^{-1} . The lowest peak at 809-722 cm^{-1} is the out-of-plane C-H benzene. The reference groups, also known as the aliphatic group, can be observed at the peaks of approximately 1456 cm^{-1} and 1376 cm^{-1} for all bituminous samples. sulfoxide functional group at wavenumbers ranging from 970 cm^{-1} to 1070 cm^{-1} , where a peak exists in this range for the control bitumen sample at 1030 cm^{-1} .

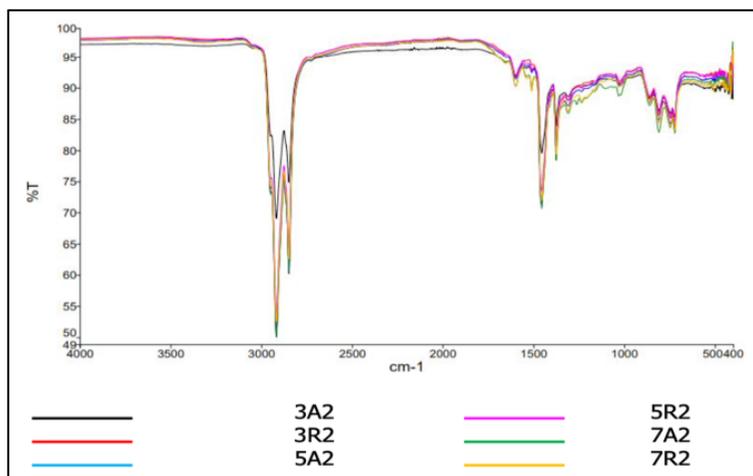


Fig. 6. Comparison of FTIR spectrum for all modified bitumen samples.

3.5 Statistical Analysis

In this particular design, the two factors were investigated based on the content of bio-oil and MDI; the percentage of bio-oil and MDI and the ratio of bio-oil to MDI. The physical properties of the bitumen; penetration, softening point and ductility were used as response variables. The result of ANOVA for responses shows that the addition and replacement of PKS bio-oil and MDI to bitumen has notable impacts on the responses with a p-value less than 0.05. P-values lower than 0.05 showed the model terms are significant. Using the correlation fit model, every parameter's individual data was analysed further. To calculate R^2 values, the correlation fit model of each graph is represented by its own equation. The modified R^2 indicates the goodness of fit of the proposed model, where R^2 quantifies the amount of variance surrounding the fitted values. High R^2 values closer to 1 indicate that the obtained data can be interpreted with a high degree of precision using linear model correlation. The higher the R^2 value, the more precise the model. In contrast, the acceptable value of R^2 is identified by the definition of the independent variables [19]. The R^2 values are listed in Table 4. All models have R^2 values greater than 0.75, indicating that the predicted and experimental outcomes are highly correlated. In this study, an R^2 greater than 0.5 is considered acceptable due to the significant variation in PKS bio-oil and MDI content as reported by Gungat [19].

Table 4. R² for statistical parameters.

Statistical Parameter	R ²
Penetration	0.9109
Softening Point	0.9039
Ductility	0.9553

3.6 Optimization of Modified Bitumen for Targeted Response

This study aimed to reach a specification limit for penetration, softening point, and ductility responses within range or better than the conventional bitumen. The optimum percentage of bio-oil and MDI (3% -7%), and the ratio of bio-oil to MDI were set to maximise from (1.0:1.0–1.0:0.6) to meet the penetration value (80–100) and softening value (45–52) with a target of minimum ductility of 100 cm. Both penetration and softening point values of the PKS bio-oil and MDI modified bitumen, are optimized using RSM within the specification of JKR's standard. The optimized result of each penetration and softening point are 92 dmm, 93 dmm, and 45 °C, respectively. However, the optimized values generated for ductility failed to satisfy the JKR's standard which is minimum distance of 100 cm. The generated values for ductility by RSM are 48.1 cm, 47,7 cm and 43.0 cm. Among these three optimum solutions, the solution with the highest desirability was selected (0.402).

4 Conclusion

This section summarised the main findings of the study. The relationship between the percentage and ratio of PKS bio-oil MDI of the modified bitumen showed that the higher the content (percentage and ratio) of PKS bio-oil and MDI the softer the bitumen grade as the mixing duration increased. The physical effect of PKS bio-oil mixed with MDI on bio-asphalt properties are identified with the physical tests consisted of penetration, softening point and ductility. Increase addition and replacement of bitumen using PKS bio-oil and MDI increased the penetration and decrease the softening and ductility values. Application of 3% (addition and replacement) of PKS bio-oil and MDI with ratios 1.0:0.6 and 1.0:1.0 reduced the penetration, softening point and ductility values. 5% and 7% (addition and replacement) of PKS bio-oil and MDI with ratio of 1.0:0.6 and 1.0:1.0 have significantly increase the penetration and lower the softening point and ductility values. For chemical effect, the functional group of modified bitumen are examined by FTIR analysis and it shows the presence of alkane group, carbonyl group, aliphatic group, aromatic group, aromatic ring and sulfoxide group. The slight differences between original bitumen and modified bitumen are influenced by the changes of chemical composition of the bitumen due the increasing percentage and ratio of PKS bio-oil and MDI. Based on the optimization of bio-asphalt mixture after the 2,4-diphenylmethane diisocyanate (MDI) has been blended with PKS bio-oil and bitumen is determined by RSM. Three solutions were generated and the solution with highest desirability was selected. The optimum percentage of bio-oil and MDI and the ratio are determined as 4% and 1.0:0.6 respectively with the desirability of 0.402.

Hence, from the physical tests, it shows that the PKS bio-oil modified bitumen required further studies on the content; both percentage and ratio. From the optimization of bio-asphalt by RSM, the suggested percentages and ratios of PKS bio-oil and MDI provided are only favourable towards penetration and softening point since they are within the JKR standard. The ductility values suggested are not within the JKR's standard. Thus, more detailed studies are required to investigate the percentage and ratio of PKS bio-oil and MDI on physical properties and optimization of bio-asphalt.

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