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Preparation of bio-bitumen by bio-oil based on free radical polymerization and production process optimization

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Abstract: Bio-oil produced during the production of biodiesel from waste cooking oil is a burden to the environment. The recycling and utilization of bio-oil as substitute for pavement bitumen may help to build an environmentally-friendly and clean infrastructure. In this study, the bio-bitumen was prepared by bio-oil based on free radical polymerization. Different kinds of bio-bitumen products were produced by reacting bio-oil with an initiator and an accelerator solution at different reaction conditions. The orthogonal experimental method was employed to determine the optimal production process of bio-bitumen by evaluating the indices of viscosity, rutting factors and fatigue factors. The test results show that the optimal mass ratio of bio-oil solution, initiator, and accelerator solution is 100 : 1 : 2. Materials with this mass ratio should react at 100 ℃ for 2 h to obtain the best bio-bitumen product. This kind of bio-bitumen product can be considered as a promising substitute for traditional petroleum bitumen.

Keywords: bio-bitumen, bio-oil, free radical polymerization, production process optimization, waste cooking oil

1 Introduction

As a residue from the crude oil refining process, traditional petroleum bitumen is widely used in the pavement construction industry. However, gradually decreasing crude oil reserves and increasingly strict environmental regulations have triggered the search for sustainable methods to produce bitumen substitutes. One of the promising methods proposed by researchers is to prepare bitumen substitutes from renewable and environmentally friendly bio-mass materials, the final product is also known as bio-bitumen (Wen et al., 2012; Fini et al., 2013; Hill et al., 2016).

Among current researches, bio-oils derived from bio-mass materials are commonly utilized to produce bio-bitumen. Bio-oil can be used as modifier, extender, and perfect substitute for bitumen based on its properties (Raouf and Williams, 2010), which significantly depend on the sources and production process (Zhang et al., 2015; Yang and You, 2015). For instance, the bio-oil derived from swine manure can improve the low-temperature properties while decrease the high-temperature grade of base bitumen (Fini et al., 2012). However, the bio-oil generated from waste wood resources can improve the high-temperature performance while sacrifice the medium and low-temperature performance of base bitumen (Yang et al., 2013). Besides, Yousefi et al. (2000) found that the bio-oil obtained from used-tire can also improve the low-temperature properties of base bitumen. Chailleux et al. (2012) produced a kind of bio-oil from microalgae, which showed thermo-dependent behavior comparable to asphalt. As for the production process of bio-oil, the commonly used methods are pyrolysis (Mohan et al., 2006) and liquefaction (Audo et al., 2015). In addition, bio-oils can also refer to some renewable waste oils, such as waste cooking oil (Sun et al., 2016a), waste lubricating oil (Villanueva et al., 2008), waste engine oil (Rubab et al., 2011), and so on.

China’s food industry produces more than 5 million tons of waste cooking oil every year, which is normally used to produce biodiesel. However, about 10% to 20% of by-products (bio-oil) can be obtained during the production of biodiesel. Although this kind of bio-oil can be used to refine glycerin, the high refining cost prevents its extensive use. In fact, most bio-oil is simply kept in factories occupying massive land resources. The leakage risk of these sites is a potential detriment to the clean and environmentally-friendly material recycling system.

There are many methods to prepare satisfactory bio-bitumen using bio-oil. The most common method is to modify base bitumen by bio-oil directly (Villanueva et al., 2008; Sun et al., 2016b; Yang et al., 2017), but the content of the bio-oil is usually very limited because of the poor high-temperature performance of bio-oil. Bio-oil can also be treated to reduce unfavorable components before being used as a modifier of base bitumen, which improves the performance of final bio-bitumen products (Zhang et al., 2017). In addition, bio-oil can also be modified by polymers (Peralta et al., 2012) or mixed with other materials, such as hard bitumen particles and resin (Sun et al., 2017), to obtain satisfactory bio-bitumen, which can be used as a perfect substitute for traditional petroleum bitumen.

Most researchers, however, have focused on the physical method to prepare bio-bitumen using bio-oil, such as physical mixing or simple modification. Few have investigated the chemical method to prepare bio-bitumen using bio-oil. This method has the potential to produce greater bio-bitumen due to strong chemical bonds in the final product. Additionally, it is also meaningful to investigate the production process of bio-bitumen, because the production process has significant influence on the performance of the final product. In this paper, a chemical method is introduced to prepare bio-bitumen using bio-oil, and the production process of bio-bitumen is also optimized based on the orthogonal experimental method.

2 Reaction mechanisms

Free radical polymerization occurs in the production process of high molecular weight bio-bitumen by low molecular weight bio-oil. The total process of free radical polymerization contains the elementary reactions of chain initiation, chain growth, and chain transfer or chain termination. These elementary reactions constitute the microscopic process of free radical polymerization. The procedure of the free radical polymerization is shown below.

First, the initiator (I) decomposes into primary free radical R^*, which has an additional reaction with the carbon-carbon double bond in a monomer to generate a monomer free radical. This process is called chain initiation (see Fig. 1).

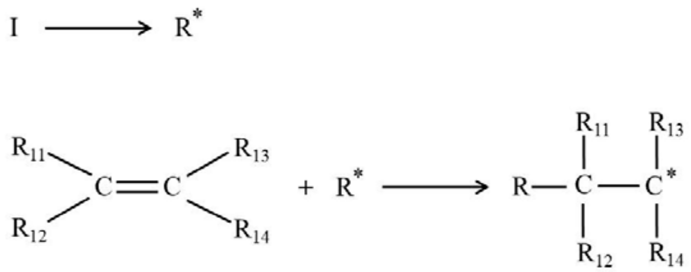


Fig. 1. Schematic presentation of chain initiation.

Second, the monomer free radical reacts with the carbon-carbon double bonds in other monomers, continuously and rapidly, to increase the chain (see Fig. 2). The active center is always at the end of the chain.

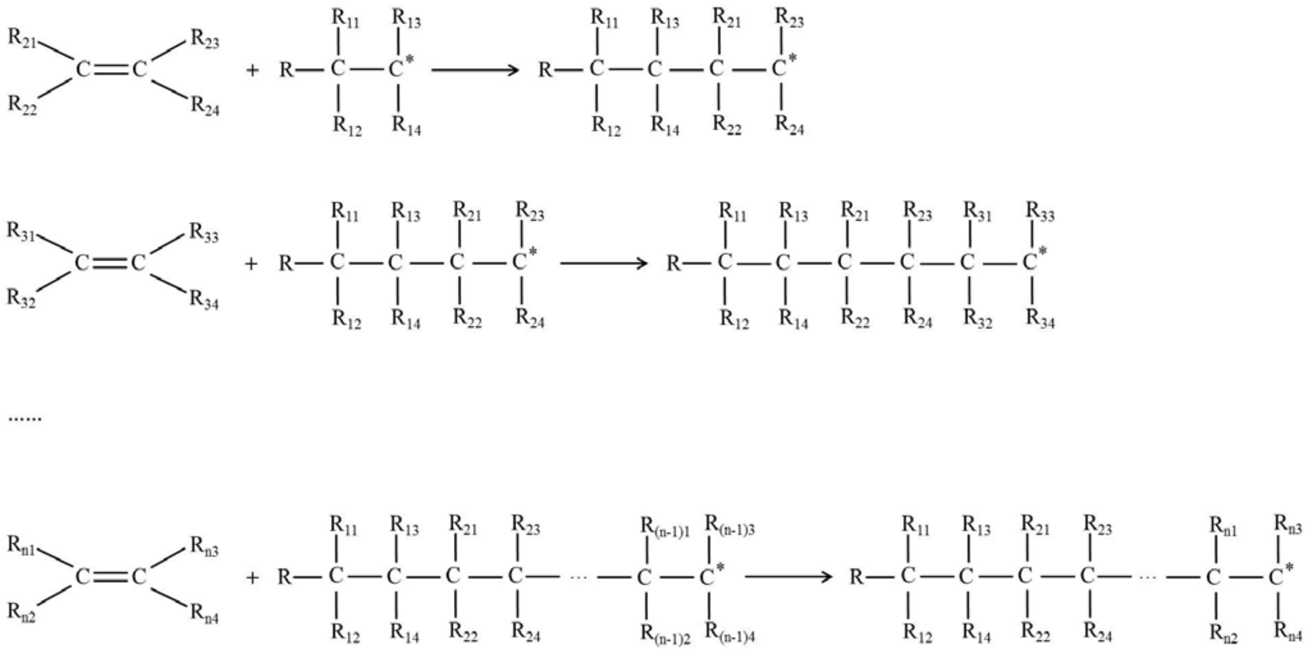


Fig. 2. Schematic presentation of chain growth.

Finally, the active chain transfers the activity to the monomer or solvent M and becomes stable, which process is called *chain transfer*. The active chain can also terminate itself to be an inactive polymer, which process is called *chain termination* (see Fig. 3).

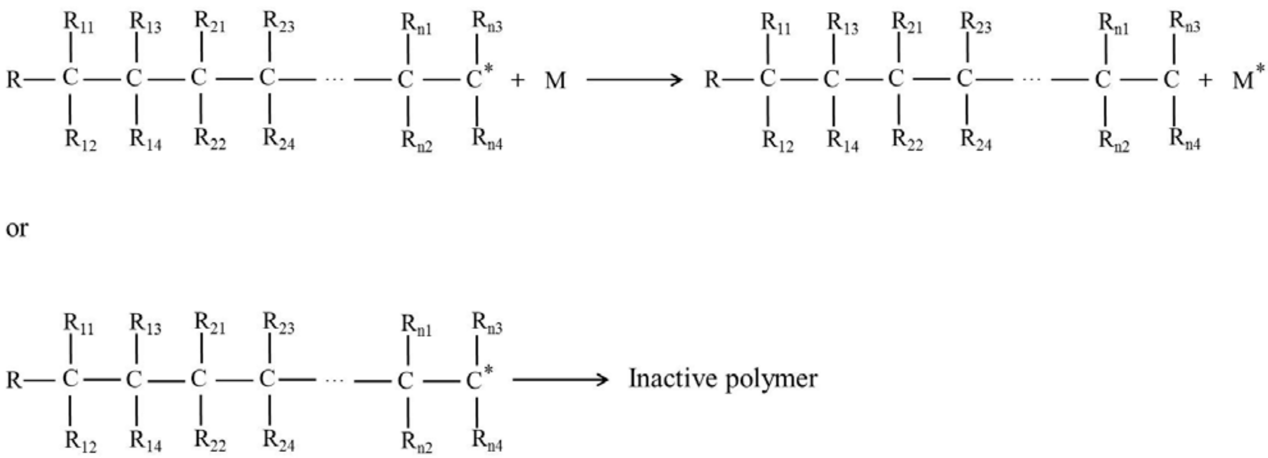


Fig. 3. Schematic presentation of chain transfer and chain termination.

3 Materials and methods

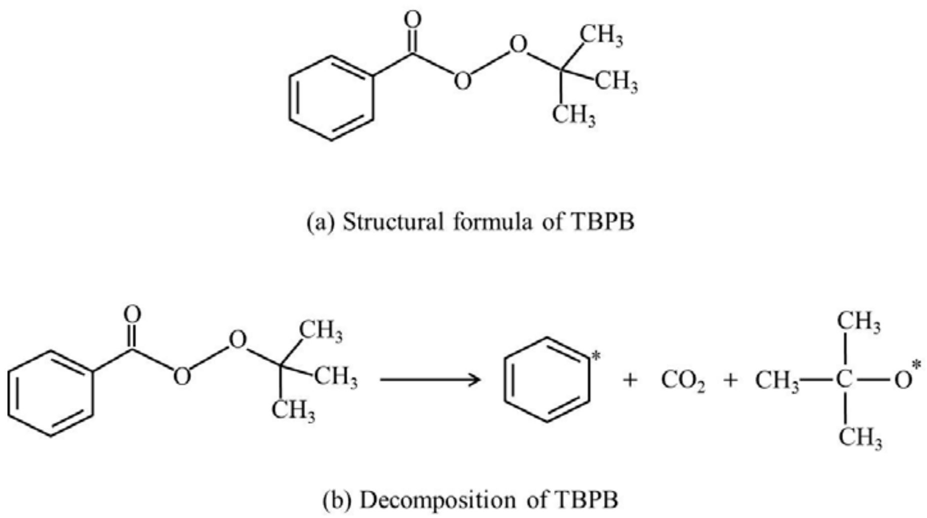
The details of the experimental materials, the preparation process of bio-bitumen, and corresponding performance evaluation methods are shown in this section.

3.1 Bio-oil

Bio-oil, a black oily liquid, is the by-product in the process of refining waste cooking oil for biodiesel. The bio-oil used in this research is the same as the one used in previous research. The detailed basic properties of bio-oil can be found in reference Sun et al. (2016a).

3.2 Initiator

The initiator used for polymerization in this research is tert-butyl peroxybenzoate (TBPB). Its Chemical Abstracts Service (CAS) number is 614-45-9. It is a clear, colorless to slightly yellow, mildly aromatic liquid. TBPB should be stored and transported as a mixture with inert solids and as solvent slurry to mitigate the explosion hazard. As an initiator, TBPB decomposes to an active free radical when heated to initiate the polymerization process. The structural formula and decomposition of TBPB is shown in Fig. 4.



(a) Structural formula of TBPB

(b) Decomposition of TBPB

Fig. 4. Structural formula and decomposition of TBPB.

3.3 Accelerator

The accelerator used for polymerization in this research is cobalt naphthenate. Its CAS number is 61789-51-3. Cobalt naphthenate is a purple to dark brown liquid that is easily ignited and burns profusely once ignited. It can also be used to prepare paint. The accelerator decreases the activation energy of the reaction to accelerate the process. The structural formula of Cobalt naphthenate is shown in Fig. 5.

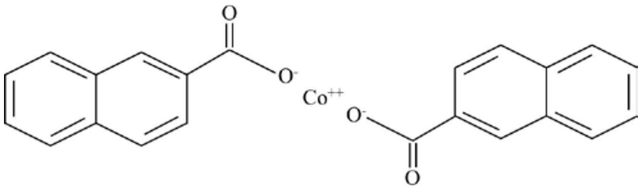


Fig. 5. Structural formula of Cobalt naphthenate.

3.4 Solvent

In order to ensure the smooth process of polymerization, styrene is introduced as a solvent. Its CAS number is 100-42-5. Styrene is a colorless to yellow oily liquid with a sweet floral odor. The existence of a solvent ensures a stable reaction environment. The structural formula of styrene is shown in the Fig. 6.

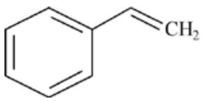


Fig. 6. Structural formula of styrene.

3.5 Bio-bitumen preparation

The preparation procedure of the bio-bitumen can be described as follows. Firstly, the bio-oil is dissolved in styrene by a mass ratio of 1 : 2 to obtain a homogenous bio-oil solution. The Cobalt naphthenate is also dissolved in styrene by a mass ratio of 8 : 92 to obtain a homogenous accelerator solution. Secondly, the bio-oil solution, initiator, and accelerator solution are mixed uniformly with a certain mass ratio. Finally, the mixed solution is added into a reactor at a certain temperature for a certain time to prepare bio-bitumen. The process of producing high molecular compounds from low molecular compounds is called *polymerization*.

In this research, the mass of the bio-oil solution was set to be 100 g, and the other reaction factors, such as the mass of the initiator, the mass of the accelerator solution, the reaction temperature, and the reaction time were designed based on the orthogonal experimental method. The levels of different factors are shown in Table 1, and the orthogonal experimental plan is shown in Table 2.

Table 1

Specific values of different levels for different factors.

Levels	Factor A Mass of initiator (g)	Factor B Mass of accelerator solution (g)	Factor C Reaction temperature (℃)	Factor D Reaction time (h)
1	1	1	85	2
2	2	2	100	4
3	3	3	115	6
4	4	4	130	8

Table 2

Orthogonal experimental plan.

No.	Levels			
	Factor A	Factor B	Factor C	Factor D
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	1	4	4	4
5	2	1	2	3
6	2	2	1	4
7	2	3	4	1
8	2	4	3	2
9	3	1	3	4
10	3	2	4	3
11	3	3	1	2
12	3	4	2	1
13	4	1	4	2
14	4	2	3	1
15	4	3	2	4
16	4	4	1	3

3.6 Methods

At first, the chemical components of bio-bitumen products were researched from the perspective of functional groups by conducting FT-IR tests. Then, suitable evaluation indices were selected to optimize the production process of bio-bitumen to ensure the performance of the final product. For bituminous binders, the rotational viscosity can be used to estimate the fluidity degree of the materials and also to investigate the handling and pumping performance of corresponding mixtures during mixing, compaction, and storage (Yao et al., 2012). In the Superpave® specification, the parameters $G^*/\sin\delta$ and $G^*\sin\delta$ (G^* is the absolute value of complex modulus and δ is the phase angle)are used to account for the contribution of binders to the rutting resistance and fatigue cracking resistance performance of mixtures, so they are also known as *rutting factor* and *fatigue factor*, respectively. Hence, the evaluation indices of viscosity, rutting factor, and fatigue factor were chosen to investigate the performance of the bio-bitumen products. According to the Chinese specification (JTG E20-2011), the methods to measure functional group, viscosity, rutting factor, and fatigue factor are shown below.

3.6.1 Fourier Transform Infrared Spectroscopy (FT-IR) test

The functional groups in the sample can be identified by conducting FT-IR test, the principle of which is that a kind specific of infrared light with a certain frequency can only be absorbed by a specific functional group. Hence, every functional group has corresponding characteristic absorption band in the IR spectrum. In the test process, the samples were dissolved in toluene and then drop-cast onto a potassium bromide (KBr) salt plate with specific thickness. In this paper, the wavenumber range was from 4000 to 400 cm^{-1}, the scan resolution was 1 cm^{-1}.

3.6.2 Rotational viscosity (RV) test

According to the standard test procedure of the RV test, the Brookfield viscometer was used to measure the rotational viscosity of bio-bitumen, which was determined by measuring the resistance of a metal spindle spinning in a container filled with test sample at specific speeds. The test temperature in this paper was 135 ℃.

3.6.3 Dynamic shear rheometer (DSR) test

To evaluate the high temperature performance of bio-bitumen, the rutting factor was measured by a DSR test. In this study, the strain level was 12%, the angular frequency was 10 rad/s, the test temperature was 64 ℃, and two 25 mm diameter metal plates with 1 mm gap were used.

In addition, the fatigue factor of bio-bitumen was measured by DSR test to investigate the fatigue performance of bio-bitumen. In this research, the strain level was 1%, the angular frequency was 10 rad/s, the test temperature was 25 ℃, and two 8 mm diameter metal plates with a 2 mm gap were used.

4 Results and discussions

In order to have a better understanding about the properties of the prepared bio-bitumen products and optimize the production process, the detailed test results and corresponding analyses are shown in this section.

4.1 Chemical components

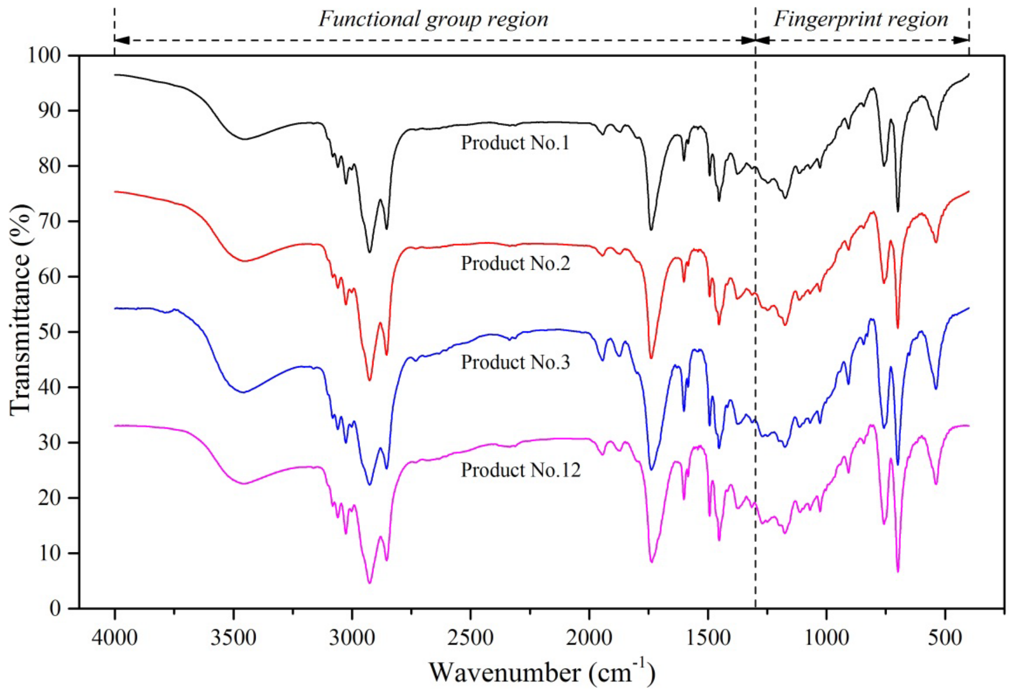


Fig. 7. IR spectra of typical bio-bitumen products.

The chemical components of bio-bitumen product are very important to its properties, so the FT-IR tests are conducted to investigate the differences of the chemical components of bio-bitumen, bio-oil, and base bitumen from the functional group point of view. The IR spectra of four typical bio-bitumen products, which have the highest overall desirability in section 4.5, are shown in Fig. 7. It can be seen that the IR spectra of bio-bitumen products are almost the same, which means the functional groups of them are almost the same.

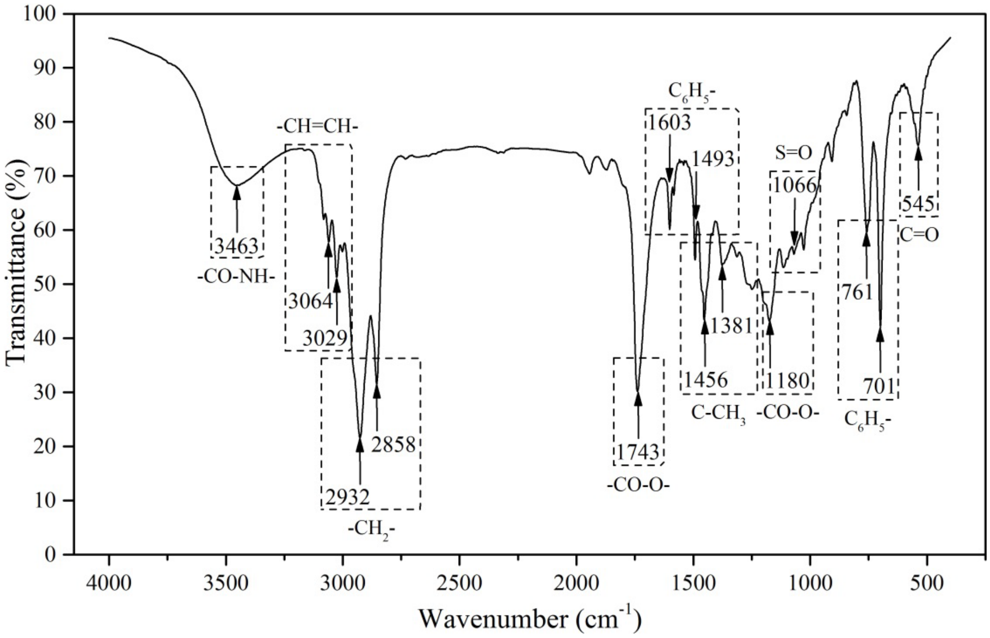


Fig. 8. Functional groups of typical bio-bitumen product.

The functional groups of a typical bio-bitumen product are shown in Fig. 8 by analyzing the corresponding IR spectra. It is obvious that the bio-bitumen consists of saturated hydrocarbons, alkenes, amides, aromatic compounds, esters, ketone compounds, and sulfinyl compounds. Combining the results from previous researches (Sun et al., 2016a), the functional groups of bio-oil, bio-bitumen, and base bitumen were compared in Fig. 9, which shows that the bio-bitumen has new components of aromatic compounds compared with bio-oil. The reason for this phenomenon is the polymerization of bio-oil initiated by TBPB. The real reactions in the polymerization process are very complex, because both bio-oil and styrene have unsaturated carbon-carbon double bond. Hence, the polymerization could happen only between bio-oil monomers, or only between styrene monomers, or between bio-oil monomers and styrene monomers. Besides, it can be seen from Fig. 9 that the bio-bitumen has new components of alkenes and esters compared with base bitumen.

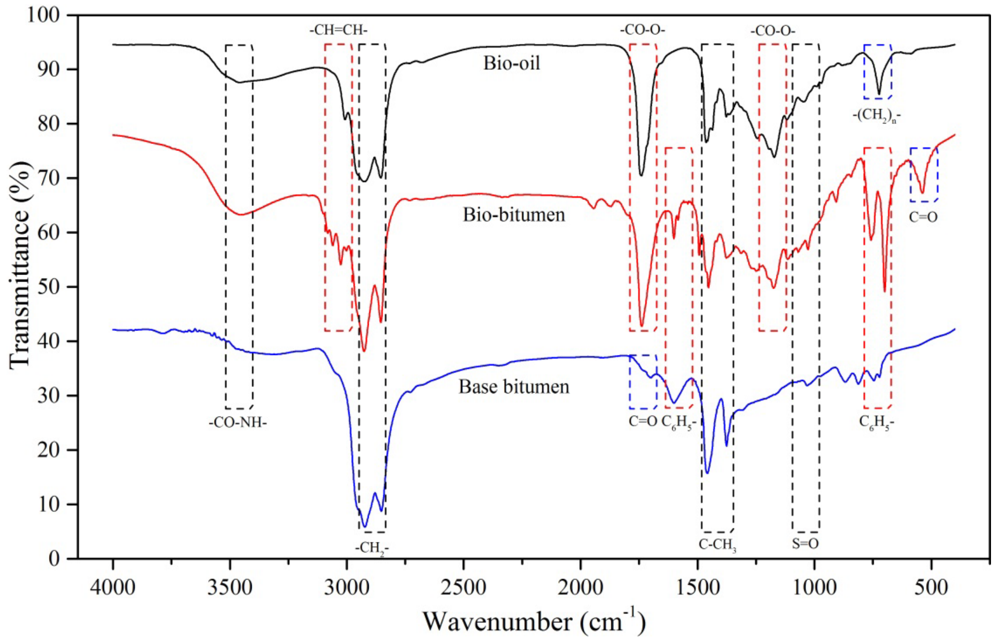


Fig. 9. Comparison of functional groups in different materials.

4.2 Viscosity values

The detailed viscosity values of bio-bitumen at 135 ℃ are shown in Appendix 1. In the table shown in Appendix 1, for a certain factor, K_i is the summation of viscosities at level i, k_i is the average value of viscosities at level i, R is the range of k values. In other words, for certain factors, the values of K and k for level i were calculated by equations (1) and (2) respectively, and the values of R were calculated by equation (3). The viscosity average values k at different levels for different factors are shown in Fig. 10.

$$K_i = \sum_{i=1}^{n} V_i \tag{1}$$

$$k_i = \frac{K_i}{n} \tag{2}$$

$$R = k_{\max} - k_{\min} \tag{3}$$

where V_i is the viscosity values at level i, n is the total number of V_i.

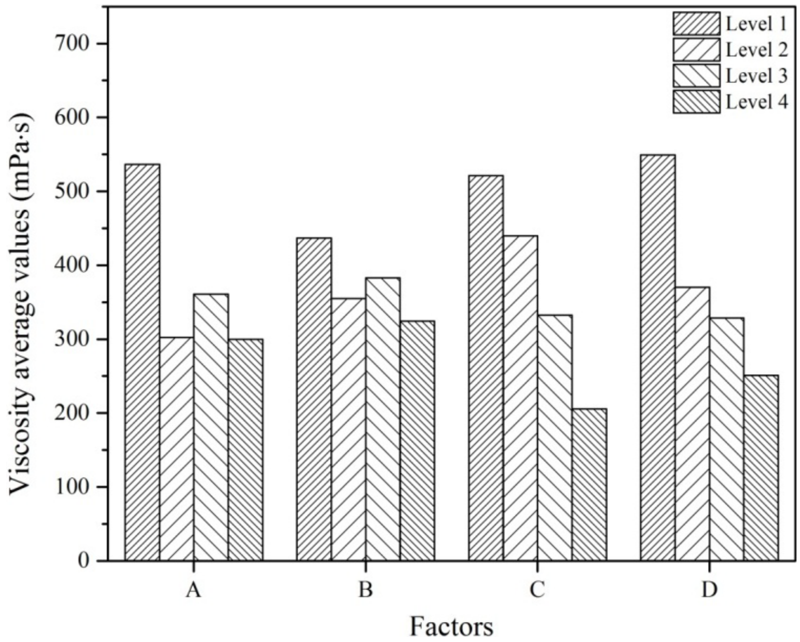


Fig. 10. Viscosity average values at different levels for different factors.

Viscosity is an index of the shear resistance ability of bitumen, and the higher the viscosity, the better the shear resistance ability. So, bio-bitumen product with higher viscosity is expected. Fig. 10 shows that, from the viscosity point of view, the optimal process for bio-bitumen production is A1B1C1D1, which means the optimal experimental materials mass ratio is bio-oil solution : initiator : accelerator solution = 100 : 1 : 1, the optimal reaction temperature is 85 ℃, and the optimal reaction time is 2 h.

4.3 Rutting factor values

The rutting factor values of bio-bitumen at 64 ℃ are shown in Appendix 2. In the table shown in Appendix 2, for a certain factor, K_i is the summation of rutting factors at level i, k_i is the average value of rutting factors at level i, and R is the range of k values. The rutting factor average values k at different levels for different factors are shown in Fig. 11.

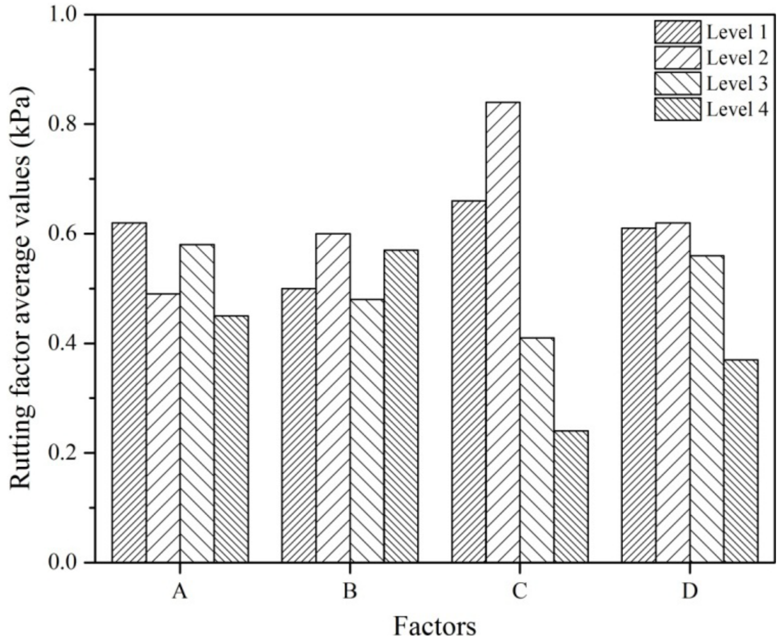


Fig. 11. Rutting factor average values at different levels for different factors.

Rutting factor is an index of the high-temperature rutting resistance performance of bitumen, and the larger the rutting factor, the better the high-temperature performance. So, bio-bitumen product with a larger rutting factor is expected. It can be seen from Fig. 11 that, from the rutting factor point of view, the optimal process for bio-bitumen production is A1B2C2D2, which means the optimal experimental materials mass ratio is bio-oil solution : initiator : accelerator solution = 100 : 1 : 2, the optimal reaction temperature is 100 ℃, and the optimal reaction time is 4 h.

4.4 Fatigue factor values

The fatigue factor values of bio-bitumen at 25 ℃ are shown in Appendix 3. In the table shown in Appendix 3, for a certain factor, K_i is the summation of fatigue factors at level *i*, k_i is the average value of fatigue factors at level *i*, and *R* is the range of *k* values. The fatigue factor average values *k* at different levels for different factors are shown in Fig. 12.

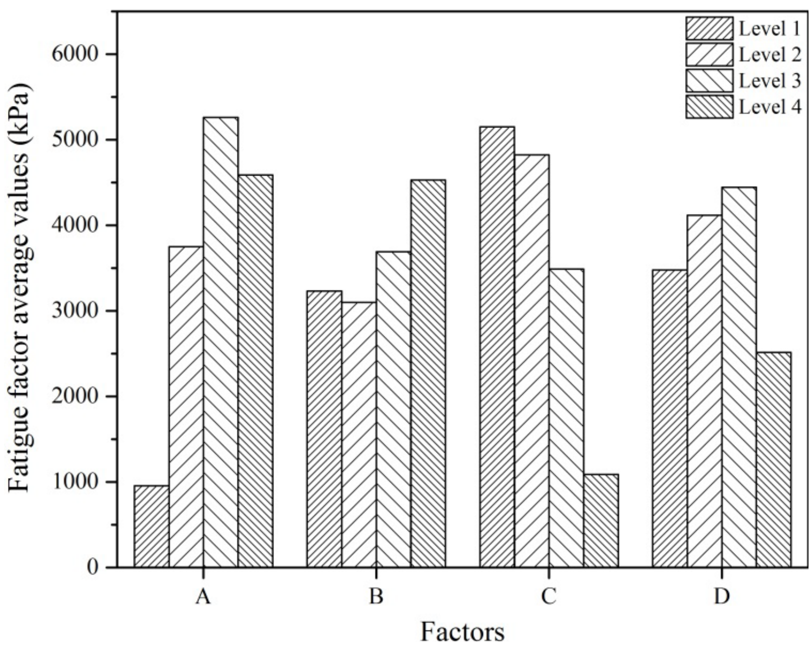


Fig. 12. Fatigue factor average values at different levels for different factors.

Fatigue factor is an index of fatigue resistance performance of bitumen, and the smaller the fatigue factor, the better the fatigue resistance performance. So, bio-bitumen product with a smaller fatigue factor is expected. Fig. 12 shows that, from the fatigue factor point of view, the optimal process for bio-bitumen production is A1B2C4D4, which means the optimal experimental materials mass ratio is bio-oil solution : initiator : accelerator solution = 100 : 1 : 2, the optimal reaction temperature is 130 ℃, and the optimal reaction time is 8 h.

4.5 Overall desirability

At first, the test values of different evaluation indices are normalized to be values between 0 and 1 based on Hassan’s mathematical transform method (Tan et al., 2013). If the performance of the product is better when the value of the evaluation index is larger, equation (4) should be employed to obtain normalized values; otherwise, equation (5) should be used.

$$NV_i = \frac{V_i - V_{\min}}{V_{\max} - V_{\min}} \tag{4}$$

$$NV_i = \frac{V_{\max} - V_i}{V_{\max} - V_{\min}} \tag{5}$$

where NV_i means the normalized value of the production process No. i for a certain evaluation index, V_i means the corresponding test value, V_{max} means the maximum value of the corresponding test values, and V_{min} means the minimum value of the corresponding test values.

The overall desirability (OD) for a certain production process is defined as the geometric mean of the corresponding normalized values of different evaluation indices, as shown in equation (6), which can comprehensively evaluate the performance of the product.

$$OD_i = \sqrt[n]{\prod_{j=1}^{n} NV_{ij}} = \sqrt[n]{NV_{i1} \cdot NV_{i2} \cdot NV_{i3} \cdots\cdots NV_{in}} \tag{6}$$

where OD_i means the overall desirability of production process No. i, NV_{ij} means normalized value of evaluation index j for production process No. i, and n means the total number of evaluation indices.

The overall desirability values of bio-bitumen performance are shown in Appendix 4. In the table shown in Appendix 4, for a certain factor, K_i is the summation of the overall desirability at level i, k_i is the average value of the overall desirability at level i, and R is the range of k values. The overall desirability average values k at different levels for different factors are shown in Fig. 13.

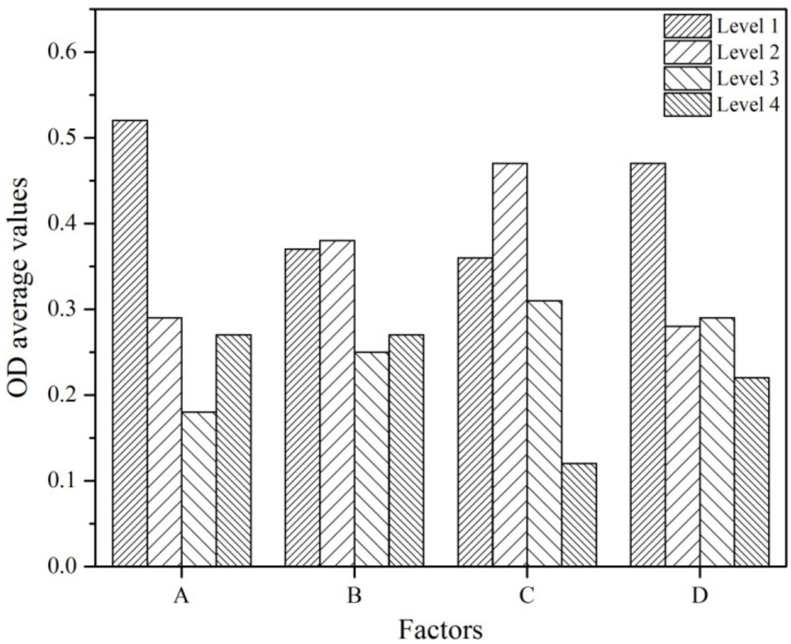


Fig. 13. Overall desirability average values at different levels for different factors.

The higher the overall desirability value, the better the overall performance. So, bio-bitumen product with a high overall desirability value is expected. It can be seen from Fig. 13 that the optimal process for bio-bitumen production is A1B2C2D1, which means the optimal experimental materials mass ratio is bio-oil solution : initiator : accelerator solution = 100 : 1 : 2, the optimal reaction temperature is 100 ℃, and the optimal reaction time is 2 h.

4.6 Performance comparison

In order to have a clear concept about the properties of bio-bitumen, the performance comparisons among bio-oil, bio-bitumen products, and base bitumen are shown in Table 3. The bio-bitumen products No.1 and No.2 are chosen for comparison because they have better overall desirability during all the bio-bitumen products prepared in this research. It is shown that the bio-bitumen products have significantly higher viscosities than bio-oil. Besides, compared with base bitumen, the No.1 product has higher viscosity and lower fatigue factor , while the No.2 product has higher viscosity and comparable rutting factor. So, compared with base bitumen, a well-prepared bio-bitumen product could have better shear resistance and fatigue resistance performance, and comparable rutting resistance performance. Therefore, the bio-bitumen product prepared by bio-oil derived from waste cooking oil in this paper is a promising substitute for traditional petroleum bitumen in pavement engineering.

Table 3

Performance comparison between bio-oil, bio-bitumen and base bitumen.

Materials	Viscosity @ 135 ℃	Rutting factor @ 64 ℃	Fatigue factor @ 25 ℃
	mPa·s	kPa	kPa
Bio-oil	5.4	—	—
Product No.1	956	0.58	409.40
Product No.2	539	1.12	1463.53
Base bitumen 1 (Pen 50)	407	1.93	672.82
Base bitumen 2 (Pen 90)	360	0.80	895.93

5 Economic analysis and industrial aspect of bio-bitumen

As discussed above, the bio-bitumen prepared by bio-oil in the laboratory showed comparable performance to base bitumen, which means that the bio-bitumen is a promising substitute for traditional petroleum bitumen. However, it is necessary and meaningful to conduct economic analysis for a new material to achieve practical application. The market prices of the experimental materials are shown in Table 4.

Table 4

Market prices of the experimental materials.

Materials	Market prices (RMB/t)	Materials	Market prices (RMB/t)
Bio-oil	3000	Styrene	8700
Cobalt naphthenate	18000	tert-Butyl peroxybenzoate	22000

Note: 1 RMB roughly equals to 0.16 USD.

Then, according to the optimized production process, the total costs for the preparation of the bio-bitumen product with certain mass can be calculated, which is shown in Table 5.

Table 5

Economic analysis on the preparation of the bio-bitumen.

Materials	Mass (g)	Costs (RMB)
Bio-oil solution (bio-oil : styrene = 1 : 2)	100	0.6819
Accelerator solution (cobalt naphthenate : styrene = 8 : 92)	2	0.01888
Initiator	1	0.02200
Produced bio-bitumen product	103	0.7228

Note: 1 RMB roughly equals to 0.16 USD.

The results show that it cost 0.7228 RMB to prepare 103 g bio-bitumen product, so the unit-price of the bio-bitumen is about 7017 RMB/t, while the unit-price of the base bitumen is about 5000 RMB/t in China. Although the unit-price of the bio-bitumen is a bit more expensive compared with the base bitumen, a partial substitute of pavement bitumen with the bio-bitumen could result in an environmentally-friendly pavement, which has ecological advantages. Previous researches have shown that the bio-oil presented in this paper can only be used as a bitumen modifier (<10% bitumen replacement), and the performance of corresponding modified bitumen is normally deteriorated. However, after conducting free radical polymerization, the produced bio-bitumen has comparable performance to base bitumen, so it could be used as a bitumen extender (25-75% bitumen replacement). For instance, if 30% of base bitumen is replaced by bio-bitumen, the unit-price of the final procuct is only increased by about 10%. Considering the limited increase of unit-price and the significant environmental advantages, the bio-bitumen is regarded as a promising substitute for tranditional petroleum bitumen in the long run.

The proposed chemical method for the preparation of bio-bitumen in this paper is easy to be achieved for both laboratory researches and industrial applications, because a reaction vessel and a temperature-controlled mechanical mixer is sufficient for the chemical reaction. It is worth mentioning that the preparation of bio-bitumen in this research is only at laboratory level, so the amount of the bio-bitumen product is only 103g once, but more products can be obtained by increasing the volume of reaction vessel. In addition, the proposed production process does not require special modification of the production equipment in waste treatment plants or refineries, but more studies are still needed to make this method suitable for industrial application.

6 Conclusions and recommendations

This paper introduced a chemical method to prepare bio-bitumen using bio-oil derived from waste cooking oil, and the corresponding optimal production process of bio-bitumen was investigated. Based on the results presented, several conclusions can be drawn:

(1) Bio-oil derived from waste cooking oil can be used to prepare bio-bitumen based on free radical polymerization, which transforms low molecular weight bio-oil to high molecular weight bio-bitumen.

(2) The optimal production process of bio-bitumen prepared by bio-oil derived from waste cooking oil is that a mixed solution consisting of bio-oil solution, initiator, and accelerator solution with mass ratio of 100 : 1 : 2 reacts at 100 ℃ for 2 h.

(3) The bio-bitumen prepared by bio-oil derived from waste cooking oil with the chemical synthetic method is a promising substitute for traditional petroleum bitumen in infrastructure engineering.

(4) The economic analysis shows that the produced bio-bitumen is a bit more expensive compared with base bitumen. However, a partial substitute of base bitumen with the bio-bitumen will lead to more environmentally-friendly

infrastructures with limited cost increase.

Based on the research presented above, there are some recommendations forfuture study:

(1)Some other types of initiator and accelerator should be included to achieve the optimal material combination for the free radical polymerization of bio-oil.

(2) More evaluation indices and test methods should be involved for other performance of bio-bitumen, such as the low-temperature cracking resistance performance, thermal stability, adhesion and cohesion performance, damage and recovery characteristics, and so on.

(3) Comprehensive mixture performance of bio-bitumen should be investigated to ensure the practical application of the produced binder material.

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Appendix 1 Viscosity values of bio-bitumen at 135 ℃

No.	Factor A	Factor B	Factor C	Factor D	Viscosity (mPa·s)
1	1	1	1	1	955.57
2	1	2	2	2	538.53
3	1	3	3	3	490.00
4	1	4	4	4	162.00
5	2	1	2	3	352.00
6	2	2	1	4	339.00
7	2	3	4	1	277.00
8	2	4	3	2	241.00
9	3	1	3	4	218.50
10	3	2	4	3	161.43
11	3	3	1	2	480.00
12	3	4	2	1	583.77
13	4	1	4	2	222.00
14	4	2	3	1	381.00
15	4	3	2	4	285.00
16	4	4	1	3	311.00
K_1	2146.10	1748.07	2085.57	2197.33	
K_2	1209.00	1419.97	1759.30	1481.53	
K_3	1443.70	1532.00	1330.50	1314.43	
K_4	1199.00	1297.77	822.43	1004.50	
k_1	536.53	437.02	521.39	549.33	
k_2	302.25	354.99	439.83	370.38	
k_3	360.93	383.00	332.63	328.61	
k_4	299.75	324.44	205.61	251.13	
R	236.78	112.58	315.78	298.21	

Appendix 2 Rutting factor values of bio-bitumen at 64 ℃

No.	Factor A	Factor B	Factor C	Factor D	Rutting factor (kPa)
1	1	1	1	1	0.58
2	1	2	2	2	1.12
3	1	3	3	3	0.50
4	1	4	4	4	0.29
5	2	1	2	3	0.88
6	2	2	1	4	0.56
7	2	3	4	1	0.25
8	2	4	3	2	0.29
9	3	1	3	4	0.30
10	3	2	4	3	0.16
11	3	3	1	2	0.83
12	3	4	2	1	1.03
13	4	1	4	2	0.25
14	4	2	3	1	0.56
15	4	3	2	4	0.32
16	4	4	1	3	0.68
K_1	2.50	2.01	2.66	2.43	
K_2	1.98	2.40	3.35	2.48	
K_3	2.32	1.90	1.64	2.22	
K_4	1.81	2.29	0.95	1.47	
k_1	0.62	0.50	0.66	0.61	
k_2	0.49	0.60	0.84	0.62	
k_3	0.58	0.48	0.41	0.56	
k_4	0.45	0.57	0.24	0.37	
R	0.17	0.12	0.60	0.25	

Appendix 3 Fatigue factor values of bio-bitumen at 25 ℃

No.	Factor A	Factor B	Factor C	Factor D	Fatigue factor (kPa)
1	1	1	1	1	409.40
2	1	2	2	2	1463.53
3	1	3	3	3	1523.79
4	1	4	4	4	429.77
5	2	1	2	3	7591.11
6	2	2	1	4	3454.08
7	2	3	4	1	473.06
8	2	4	3	2	3480.12
9	3	1	3	4	2958.57
10	3	2	4	3	1485.12
11	3	3	1	2	9559.45
12	3	4	2	1	7032.89
13	4	1	4	2	1963.93
14	4	2	3	1	5993.01
15	4	3	2	4	3210.18
16	4	4	1	3	7178.44
K_1	3826.49	12923.01	20601.37	13908.36	
K_2	14998.37	12395.74	19297.71	16467.04	
K_3	21036.03	14766.47	13955.49	17778.45	
K_4	18345.55	18121.22	4351.87	10052.59	
k_1	956.62	3230.75	5150.34	3477.09	
k_2	3749.59	3098.93	4824.43	4116.76	
k_3	5259.01	3691.62	3488.87	4444.61	
k_4	4586.39	4530.30	1087.97	2513.15	
R	4302.39	1431.37	4062.37	1931.46	

Appendix 4 Overall desirability values of bio-bitumen performance

No.	Factor A	Factor B	Factor C	Factor D	Overall desirability
1	1	1	1	1	0.761
2	1	2	2	2	0.749
3	1	3	3	3	0.506
4	1	4	4	4	0.046
5	2	1	2	3	0.338
6	2	2	1	4	0.397
7	2	3	4	1	0.239
8	2	4	3	2	0.205
9	3	1	3	4	0.194
10	3	2	4	3	0.000
11	3	3	1	2	0.000
12	3	4	2	1	0.511
13	4	1	4	2	0.180
14	4	2	3	1	0.355
15	4	3	2	4	0.262
16	4	4	1	3	0.299
K_1	2.06	1.47	1.46	1.87	
K_2	1.18	1.50	1.86	1.13	
K_3	0.70	1.01	1.26	1.14	
K_4	1.10	1.06	0.47	0.90	
k_1	0.52	0.37	0.36	0.47	
k_2	0.29	0.38	0.47	0.28	
k_3	0.18	0.25	0.31	0.29	
k_4	0.27	0.27	0.12	0.22	
R	0.34	0.12	0.35	0.24	