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

Zhaojie Sun^{1,2}, Junyan Yi^{1,*}, Decheng Feng^{1,*}, Cor Kasbergen², Athanasios Scarpas², Yiming
Zhu¹

1. School of Transportation Science and Engineering, Harbin Institute of Technology, Harbin,
150090, China

2. Faculty of Civil Engineering and Geosciences, Delft University of Technology, Delft, 2628
CN, The Netherlands

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 °C 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

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

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

61 There are many methods to prepare satisfactory bio-bitumen using bio-oil. The
62 most common method is to modify base bitumen by bio-oil directly (Villanueva et al.,
63 2008; Sun et al., 2016b; Yang et al., 2017), but the content of the bio-oil is usually
64 very limited because of the poor high-temperature performance of bio-oil. Bio-oil can
65 also be treated to reduce unfavorable components before being used as a modifier of
66 base bitumen, which improves the performance of final bio-bitumen products (Zhang
67 et al., 2017). In addition, bio-oil can also be modified by polymers (Peralta et al., 2012)
68 or mixed with other materials, such as hard bitumen particles and resin (Sun et al.,
69 2017), to obtain satisfactory bio-bitumen, which can be used as a perfect substitute for
70 traditional petroleum bitumen.

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

78 prepare bio-bitumen using bio-oil, and the production process of bio-bitumen is also
79 optimized based on the orthogonal experimental method.

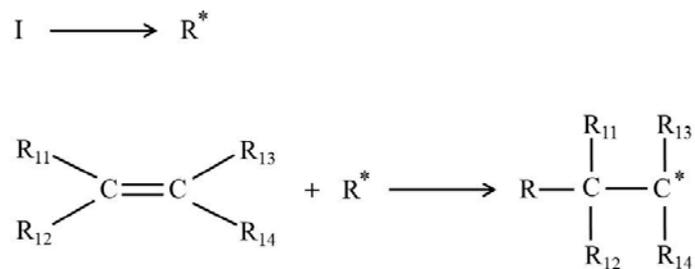
80 **2 Reaction mechanisms**

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

87

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

91



92

93

Fig. 1. Schematic presentation of chain initiation.

94

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

98

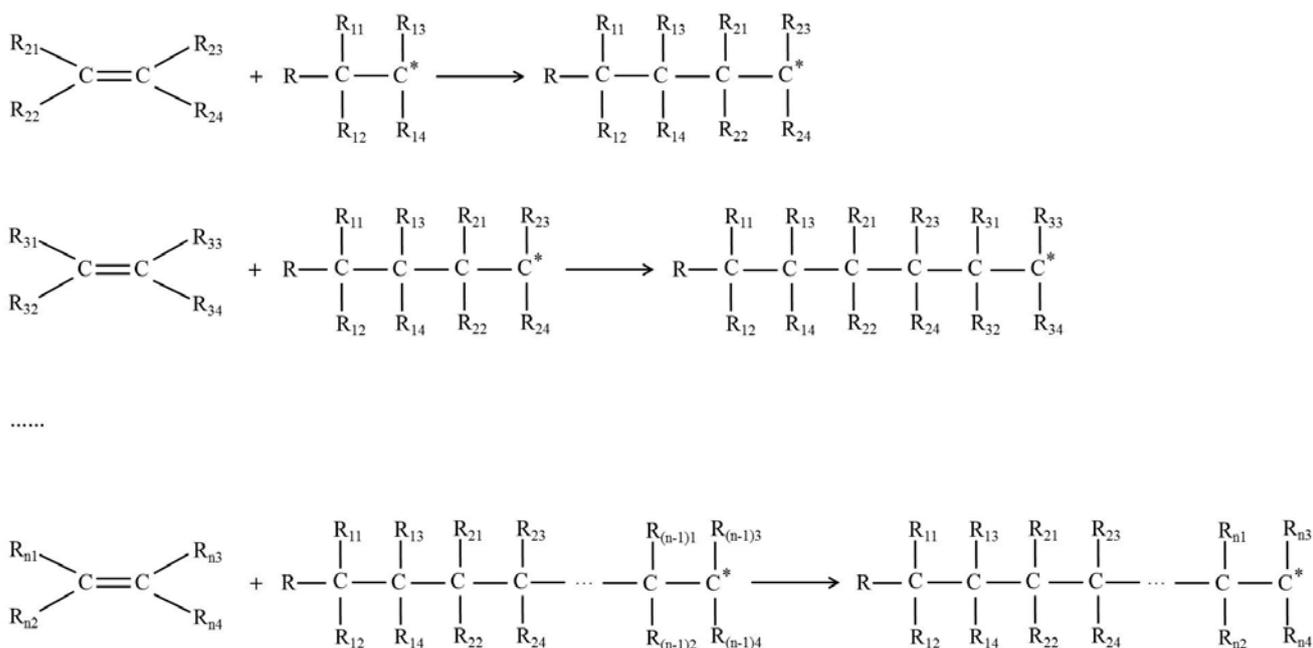
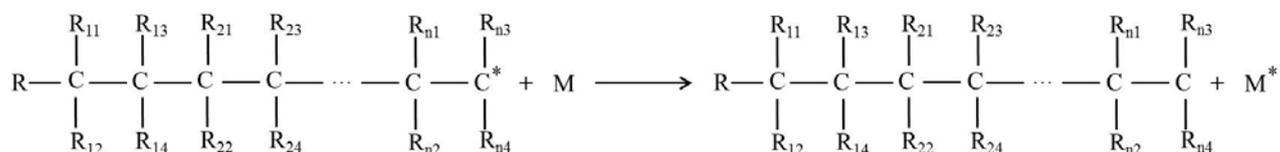


Fig. 2. Schematic presentation of chain growth.

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).



or

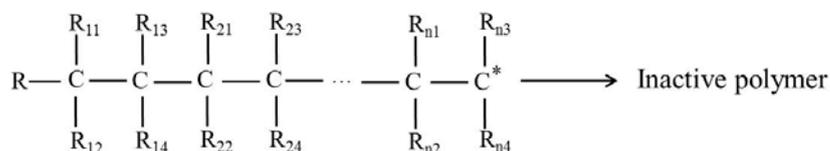


Fig. 3. Schematic presentation of chain transfer and chain termination.

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.

114 3.1 Bio-oil

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

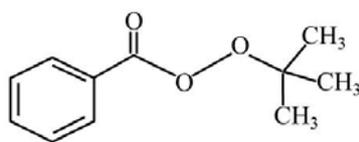
119

120 3.2 Initiator

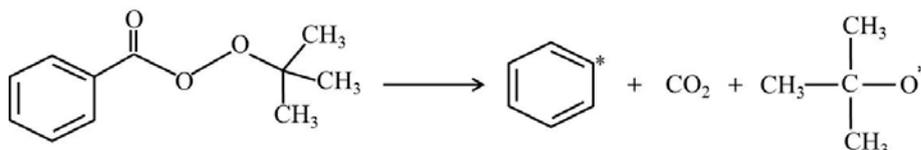
121

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

129



(a) Structural formula of TBPB



(b) Decomposition of TBPB

130

131

Fig. 4. Structural formula and decomposition of TBPB.

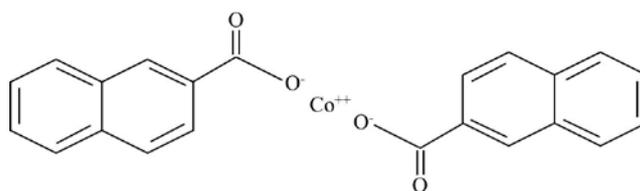
132

133 3.3 Accelerator

134

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

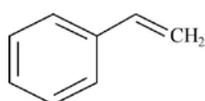
140



141
142 Fig. 5. Structural formula of Cobalt naphthenate.
143

144 3.4 Solvent

145
146 In order to ensure the smooth process of polymerization, styrene is introduced as
147 a solvent. Its CAS number is 100-42-5. Styrene is a colorless to yellow oily liquid
148 with a sweet floral odor. The existence of a solvent ensures a stable reaction
149 environment. The structural formula of styrene is shown in the Fig. 6.
150



151
152 Fig. 6. Structural formula of styrene.
153

154 3.5 Bio-bitumen preparation

155
156 The preparation procedure of the bio-bitumen can be described as follows. Firstly,
157 the bio-oil is dissolved in styrene by a mass ratio of 1 : 2 to obtain a homogenous
158 bio-oil solution. The Cobalt naphthenate is also dissolved in styrene by a mass ratio of
159 8 : 92 to obtain a homogenous accelerator solution. Secondly, the bio-oil solution,
160 initiator, and accelerator solution are mixed uniformly with a certain mass ratio.
161 Finally, the mixed solution is added into a reactor at a certain temperature for a certain
162 time to prepare bio-bitumen. The process of producing high molecular compounds
163 from low molecular compounds is called *polymerization*.

164 In this research, the mass of the bio-oil solution was set to be 100 g, and the
165 other reaction factors, such as the mass of the initiator, the mass of the accelerator
166 solution, the reaction temperature, and the reaction time were designed based on the
167 orthogonal experimental method. The levels of different factors are shown in Table 1,
168 and the orthogonal experimental plan is shown in Table 2.
169
170
171
172
173
174

175 **Table 1**

176 Specific values of different levels for different factors.

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

177

178 **Table 2**

179 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

180

181 *3.6 Methods*

182

183 At first, the chemical components of bio-bitumen products were researched from
 184 the perspective of functional groups by conducting FT-IR tests. Then, suitable
 185 evaluation indices were selected to optimize the production process of bio-bitumen
 186 to ensure the performance of the final product. For bituminous binders, the rotational
 187 viscosity can be used to estimate the fluidity degree of the materials and also to
 188 investigate the handling and pumping performance of corresponding mixtures during
 189 mixing, compaction, and storage (Yao et al., 2012). In the Superpave® specification,

190 the parameters $G^*/\sin\delta$ and $G^*\sin\delta$ (G^* is the absolute value of complex
191 modulus and δ is the phase angle) are used to account for the contribution of
192 binders to the rutting resistance and fatigue cracking resistance performance of
193 mixtures, so they are also known as *rutting factor* and *fatigue factor*, respectively.
194 Hence, the evaluation indices of viscosity, rutting factor, and fatigue factor were
195 chosen to investigate the performance of the bio-bitumen products. According to the
196 Chinese specification (JTG E20-2011), the methods to measure functional group,
197 viscosity, rutting factor, and fatigue factor are shown below.

198

199 *3.6.1 Fourier Transform Infrared Spectroscopy (FT-IR) test*

200

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

208

209 *3.6.2 Rotational viscosity (RV) test*

210

211 According to the standard test procedure of the RV test, the Brookfield
212 viscometer was used to measure the rotational viscosity of bio-bitumen, which was
213 determined by measuring the resistance of a metal spindle spinning in a container
214 filled with test sample at specific speeds. The test temperature in this paper was
215 135 °C.

216

217 *3.6.3 Dynamic shear rheometer (DSR) test*

218

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

223

224 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

225 was 1%, the angular frequency was 10 rad/s, the test temperature was 25 °C, and
226 two 8 mm diameter metal plates with a 2 mm gap were used.

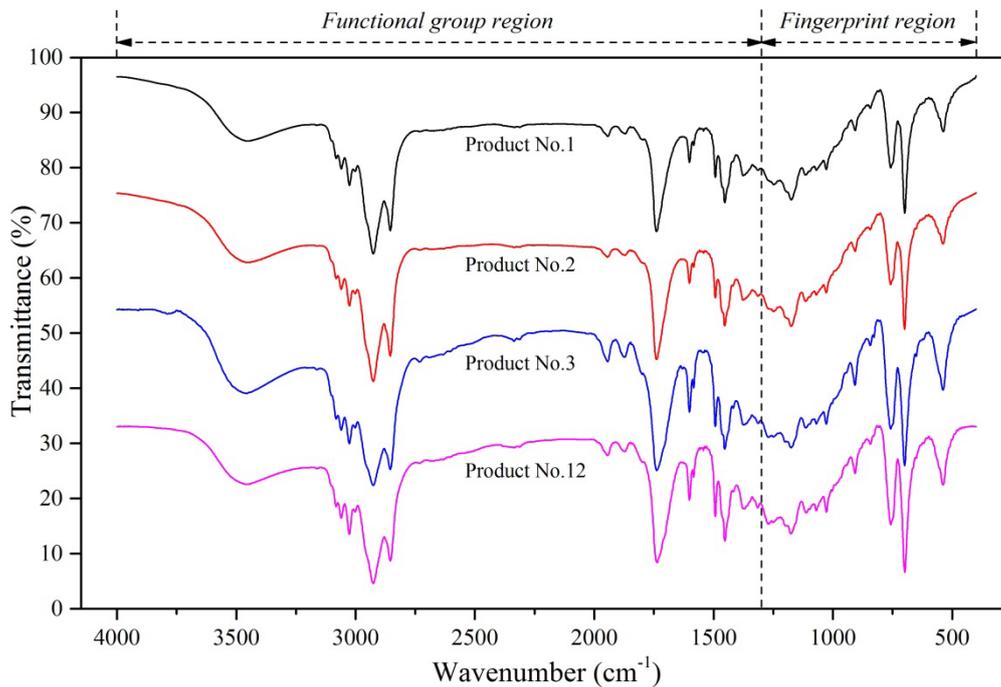
227

228 **4 Results and discussions**

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

232 *4.1 Chemical components*

233



234

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

236

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

244

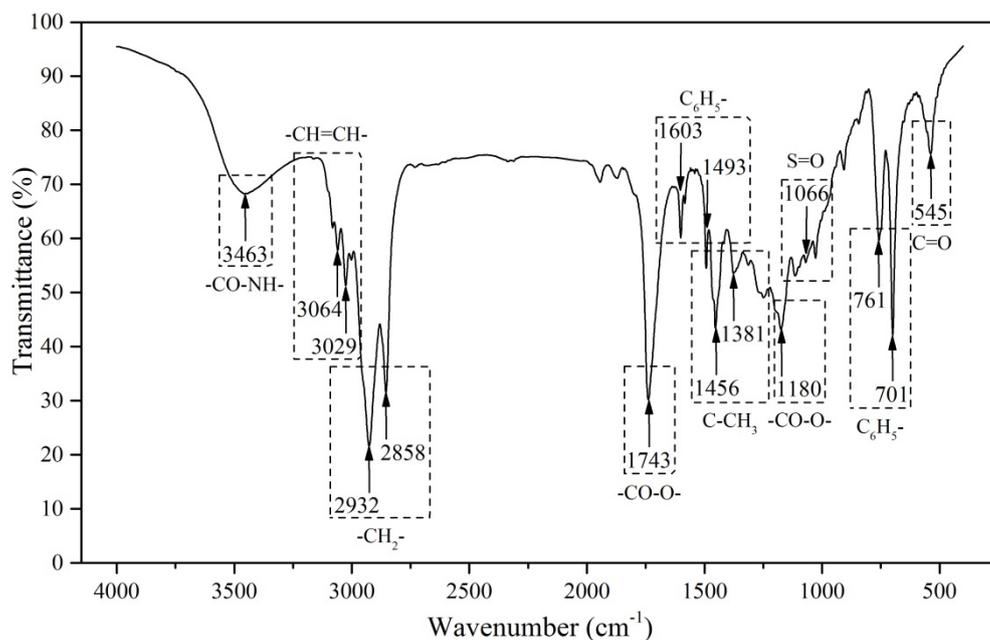


Fig. 8. Functional groups of typical bio-bitumen product.

245

246

247

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

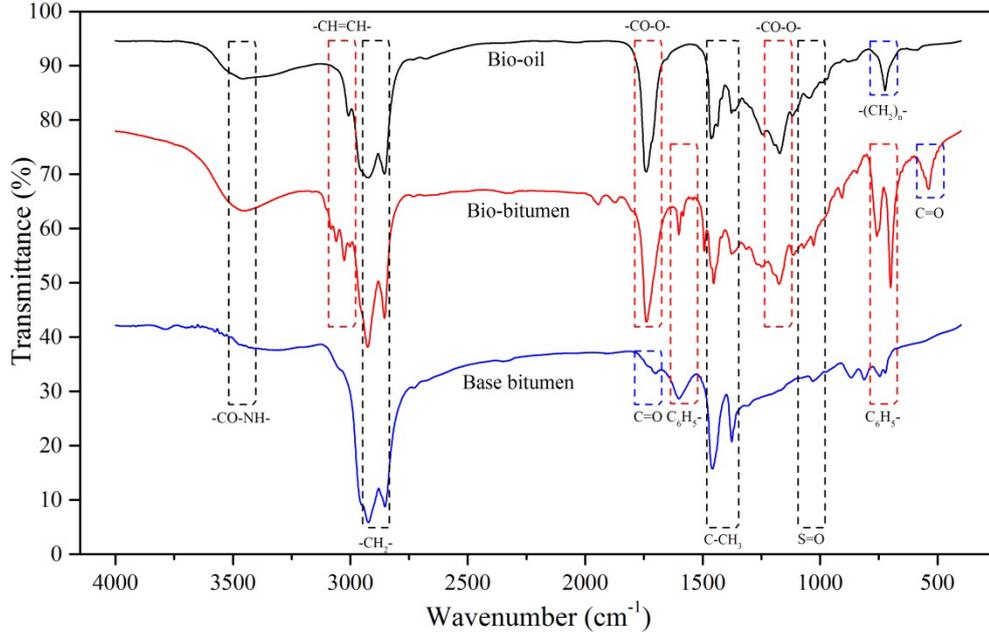


Fig. 9. Comparison of functional groups in different materials.

4.2 Viscosity values

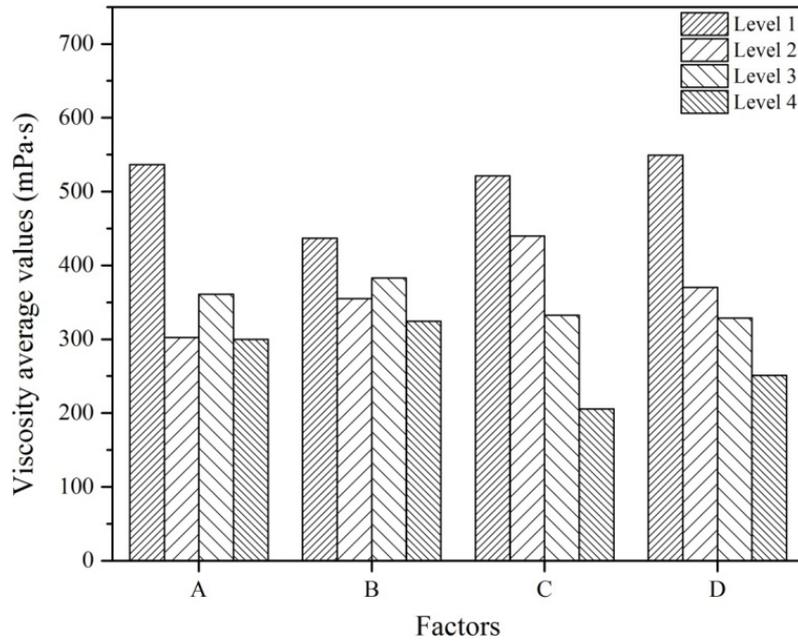
The detailed viscosity values of bio-bitumen at 135 °C are shown in Appendix 1. In the table shown in Appendix 1, for a certain factor, K_i is the summation of viscosities at level i , k_i is the average value of viscosities at level i , R is the range of k values. In other words, for certain factors, 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.

$$K_i = \sum_{i=1}^n V_i \quad (1)$$

$$k_i = \frac{K_i}{n} \quad (2)$$

$$R = k_{\max} - k_{\min} \quad (3)$$

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



278

279

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

280

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289

4.3 Rutting factor values

290

291

292

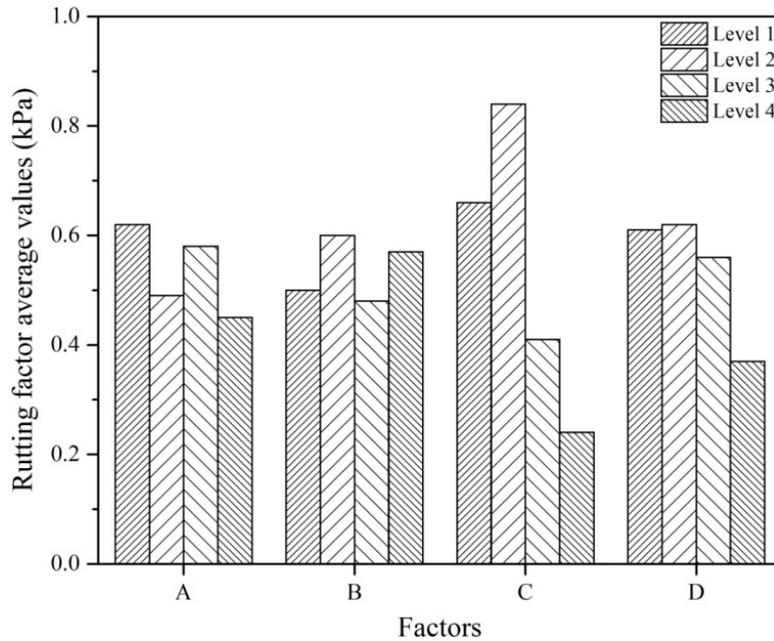
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294

295

296

The rutting factor values of bio-bitumen at 64 °C 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.



297

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

299

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

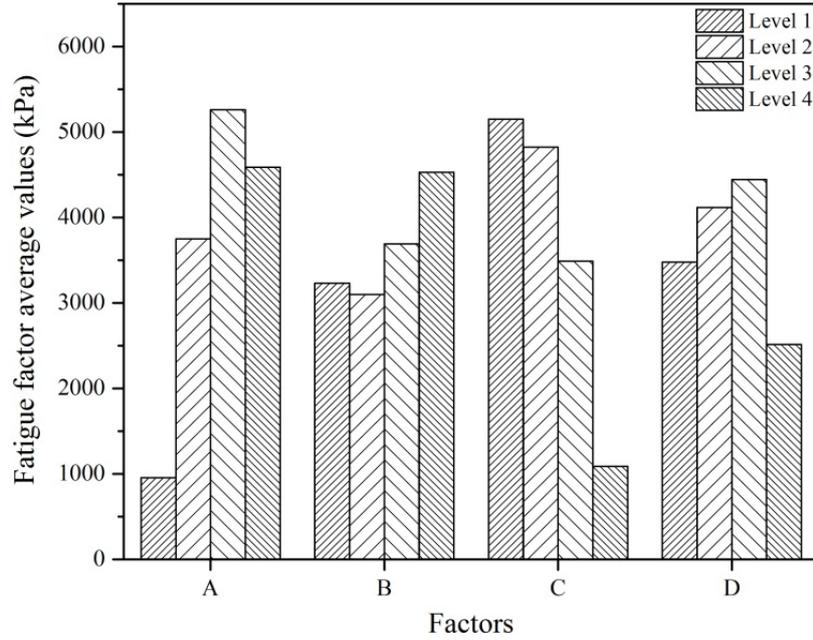
307

308 4.4 Fatigue factor values

309

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

315



316

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

318

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

326

327 4.5 Overall desirability

328

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

334

$$NV_i = \frac{V_i - V_{\min}}{V_{\max} - V_{\min}} \quad (4)$$

335

$$NV_i = \frac{V_{\max} - V_i}{V_{\max} - V_{\min}} \quad (5)$$

336

where NV_i means the normalized value of the production process No. i for a certain

337 evaluation index, V_i means the corresponding test value, V_{\max} means the maximum
 338 value of the corresponding test values, and V_{\min} means the minimum value of the
 339 corresponding test values.

340

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

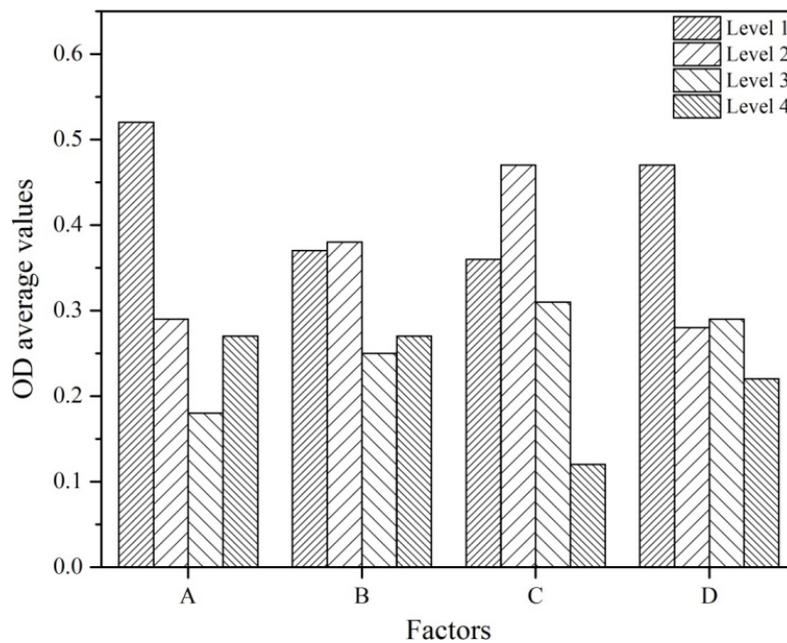
$$345 \quad OD_i = \sqrt[n]{\prod_{j=1}^n NV_{ij}} = \sqrt[n]{NV_{i1} \cdot NV_{i2} \cdot NV_{i3} \cdot \dots \cdot NV_{in}} \quad (6)$$

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

349

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

355



356

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

358

359 The higher the overall desirability value, the better the overall performance. So,
 360 bio-bitumen product with a high overall desirability value is expected. It can be seen
 361 from Fig. 13 that the optimal process for bio-bitumen production is A1B2C2D1,
 362 which means the optimal experimental materials mass ratio is bio-oil solution :
 363 initiator : accelerator solution = 100 : 1 : 2, the optimal reaction temperature is
 364 100 °C, and the optimal reaction time is 2 h.

365

366 *4.6 Performance comparison*

367

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

381 **Table 3**

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

Materials	Viscosity @ 135 °C	Rutting factor @	Fatigue factor @
	mPa·s	64 °C kPa	25 °C 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

383

384 **5 Economic analysis and industrial aspect of bio-bitumen**

385 As discussed above, the bio-bitumen prepared by bio-oil in the laboratory

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

390

391 **Table 4**

392 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

393 Note: 1 RMB roughly equals to 0.16 USD.

394

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

398

399 **Table 5**

400 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

401 Note: 1 RMB roughly equals to 0.16 USD.

402

403 The results show that it cost 0.7228 RMB to prepare 103 g bio-bitumen product,
 404 so the unit-price of the bio-bitumen is about 7017 RMB/t, while the unit-price of the
 405 base bitumen is about 5000 RMB/t in China. Although the unit-price of the
 406 bio-bitumen is a bit more expensive compared with the base bitumen, a partial
 407 substitute of pavement bitumen with the bio-bitumen could result in an
 408 environmentally-friendly pavement, which has ecological advantages. Previous
 409 researches have shown that the bio-oil presented in this paper can only be used as a
 410 bitumen modifier (<10% bitumen replacement), and the performance of

411 corresponding modified bitumen is normally deteriorated. However, after conducting
412 free radical polymerization, the produced bio-bitumen has comparable performance
413 to base bitumen, so it could be used as a bitumen extender (25-75% bitumen
414 replacement). For instance, if 30% of base bitumen is replaced by bio-bitumen, the
415 unit-price of the final product is only increased by about 10%. Considering the
416 limited increase of unit-price and the significant environmental advantages, the
417 bio-bitumen is regarded as a promising substitute for traditional petroleum bitumen
418 in the long run.

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

429 **6 Conclusions and recommendations**

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

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

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

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

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

446 infrastructures with limited cost increase.

447

448 Based on the research presented above, there are some recommendations
449 for future study:

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

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

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

458

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530

Appendix 1 Viscosity values of bio-bitumen at 135 °C

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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	

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Appendix 2 Rutting factor values of bio-bitumen at 64 °C

535

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	

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Appendix 3 Fatigue factor values of bio-bitumen at 25 °C

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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	

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Appendix 4 Overall desirability values of bio-bitumen performance

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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	

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