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Kinetic Analysis of Bio-Oil Aging by Using Pattern Search Method

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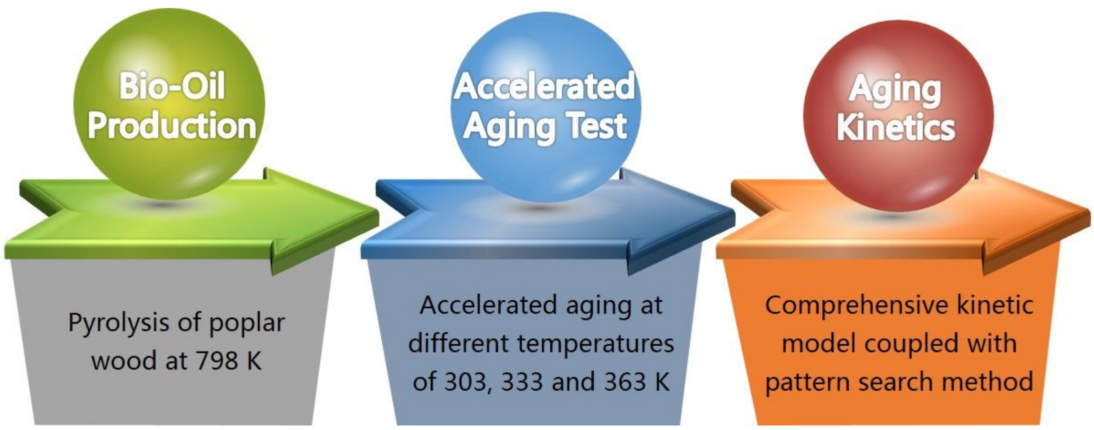
Abstract

Bio-oil derived from fast pyrolysis of lignocellulosic biomass is unstable, and aging would occur during its storage, handling, and transportation. The kinetic analysis of bio-oil aging is fundamental for the investigation of bio-oil aging mechanisms and the utilization of bio-oil as bio-fuels, bio-materials or bio-chemicals. The aging kinetic experiments of bio-oil from poplar wood pyrolysis were conducted at different aging temperatures of 303, 333, 353 and 363 K for different specified periods of time in capped glass vessels. The traditional method with two separated fittings was employed to fit experimental data, and the results indicated that the obtained kinetic parameters could not fit the experimental data well. An advanced approach for kinetic modeling of bio-oil aging has been developed by simultaneously processing experimental data at different aging temperatures and using the pattern search method. The aging kinetic model with the optimized parameters predicted the aging kinetic experimental data of the bio-oil sample very well for different aging temperatures.

Keywords: Bio-Oil; Aging Kinetics; Viscosity; Weight-Average Molecular Weight; Pattern Search Method

Graphical abstract



1 Introduction

China is facing the shortage of liquid fuels which are mainly derived from petroleum [1, 2]. Bio-oil from biomass pyrolysis can be utilized as a promising intermediate for producing transportation fuels to replace petroleum-derived liquid fuels [3]. Bio-oil contains a considerable amount of oxygen due to the presence of oxygenated compounds, which results in a low energy density [4]. It contains relatively little sulfur and nitrogen [5]. While crude oil composes of hydrocarbon deposits and other organic materials and contains an amount of sulfur, which is an undesirable contaminant because it generates sulfur oxides when burned [6]. Bio-oil has some certain advantages when it is used as a biofuel [7-9]: (1) cost efficiency, (2) easy excess to source, (3) renewability, (4) greenhouse gases reduction, (5) economic security, and (6) reduction of reliance on foreign oil. And the bio-oil heavy fraction has similar components and physicochemical properties as bitumen, such as saturated, aromatic and polar compounds as well as asphaltene [10]. Therefore, the utilization of bio-oil as a bio-asphalt or an additive for asphalt becomes very promising [10-13].

However, bio-oil is chemically and thermally unstable during storage, handling, and transportation, which limits the utilization of bio-oil [14-16]. Aged bio-oil typically shows phase separation, increased viscosity, average molecular weight and water content [17]. The aging phenomena are mainly caused by the evaporation of light volatile components, and the condensation, polymerization, esterification and oxidative reactions occurring among bio-oil components [18].

From the literature review, most recent studies on bio-oil aging were related to investigating aging process parameter effects, characterizing changes in physicochemical properties of bio-oils and seeking approaches to slow down the aging rate of bio-oils [16, 17].

The comprehensive understanding on bio-oil aging kinetics is helpful to determine the aging rate and the important properties of bio-oil under different aging periods, and predict the required time to reach different degrees of aging, which is important for the application of bio-oil as a bio-fuel, bio-chemical or bio-material and for the efficiency verification of various approaches to slow down bio-oil aging rate [19, 20]. The aging kinetic parameters including aging activation energy and frequency factor obtained from the kinetic modeling of bio-oil aging are very important for the quantitative interpretation of bio-oil aging behaviors [21]. The aging activation energy can be used to evaluate the performance for asphalt [22], since bio-oil has the possibility to use as an asphalt substitute [23, 24].

Several studies were carried out on the kinetic modeling of bio-oil aging [25-27]. In those studies, an exponential equation was generally used to describe the change in bio-oil's properties with respect to aging time, and the effect of other factors on aging was not considered. And the corresponding kinetic method for bio-oil aging is unable to provide accurate aging kinetic parameters, which will be discussed in detail later.

The main aim of this paper is to investigate the aging behaviors of bio-oil from poplar wood pyrolysis and to develop an advanced procedure for kinetic modeling of bio-oil aging.

2 Experiments and analytical methods

The bio-oil samples were obtained from poplar wood pyrolysis at 798 K in a fluidized-bed reactor with a capacity of 5 kg h^{-1}. The experimental setup for the production of bio-oil was described in detail in an earlier publication [28]. The collected liquid contained some quench medium and water. The collected liquid was centrifuged for 30 minutes at 4000 rpm in order to remove them [29]. After centrifugation, the bio-oil samples were immediately placed in capped glass vessels at atmospheric pressure and then stored in a forced-air oven [30]. The bio-oil samples were stored at the aging temperatures of 303, 333, 353, and 363 K for 90 days, 10 days, 60 hours and 24 hours, respectively. The pH value, water content, viscosity, average molecular weight, higher heating value (HHV) of the fresh and aged bio-oil sample were measured. The tests were repeated in triplicate and the average value was used for further analysis. Some experimental data will be used to estimate the aging kinetic parameters, and the other experimental data will be used to determine the validity of the aging kinetic model.

The water content of the bio-oil sample was determined by Karl Fischer titration in accordance with ASTM E203-08.. The bio-oil samples' pH values were determined at room temperature using a digital pH probe (Accumet model 8250, Fisher Scientific) in accordance with ASTM E70 - 07. The HHV of the bio-oil sample was obtained using an oxygen bomb calorimeter (XRY-1B, Shanghai Changji Geological Instruments Co., Ltd., China) in accordance with ASTM E711-81. The bio-oil's viscosity was measured using a rotational viscometer (Brookfield viscometer model DV-Ⅱ+ Pro, Ametek.Inc, USA) in accordance with ASTM D2983 - 19.

The molecular weight and its distribution of the fresh and aged bio-oil samples were analyzed using gel permeation chromatography (GPC, HLC-8321GPC/HT, Tosoh, Japan) equipped with a refractive index (RI), an ultraviolet (UV) detector and a sample pretreatment system. Two Agilent PLgel columns (3μm 100 Å 300 × 7.5 mm) and one Mesopore column (300 × 7.5 mm) were coupled in series. Tetrahydrofuran (THF), a suitable solvent for the GPC analysis of bio-oil [31], was used as the solvent at 1 mL min^{-1}. The GPC analyses of bio-oil samples were performed in accordance with ASTM D6474 - 12. Before GPC analysis, each bio-oil sample was dissolved in THF and filtered using a 0.45-μm syringe filter. All of the samples were found in the mobile phase (THF). When the molecular weight distribution is obtained, the average molecular weight can be calculated[32, 33]. In this study, the weight-average molecular weight was used:

$$\mathrm{MW}=\frac{\sum_i w_i \mathrm{M}_i}{\sum_i w_i} \qquad (1)$$

where w_i and M_i are the weight fraction and molecular weight of the i-th component in bio-oil, respectively.

3 Traditional method for aging kinetic analysis

The common aging kinetic models are expressed in terms of change in viscosity with the form of exponential functions [25, 27]. The bio-oils contains many chemical compounds mainly including phenolic components, alcohols, acids, aldehydes, ketones, esters, anhydrosugars, furans and oligomers [33, 34]. The compositions and physicochemical properties of bio-oils are subject to change with aging time and temperature [35]. In addition to increased viscosity, aging can result in increasing average molecular weight, which indicates the average length of the bio-oil component's polymer chains [33]. According to previous studies [36, 37],the aged bio-oil's weight-average molecular weight shows a positive correlation with its viscosity.

According to the aging kinetic model based on the change in viscosity, the molecular weight based aging model can be obtained:

$$\mathrm{MW}(t)=\mathrm{MW}_0+(\mathrm{MW}_\infty-\mathrm{MW}_0)\left[1-\exp(-k\cdot t)\right] \qquad (2)$$

In the above equation, t is the time, MW(t) is the weight-average molecular weight at the time t, MW_0 is the initial weight-average molecular weight, MW_∞ is the infinite time steady-state weight-average molecular weight, and k is the aging kinetic rate constant, which is dependent on the aging temperature [38]:

$$k=k_0\exp\left(-\frac{E_a}{R\cdot T_a}\right) \qquad (3)$$

where k_0 is the pre-exponential factor of Arrhenius (s^{-1}), E_a is the aging activation energy (J mol^{-1}), T_a is the aging temperature, and R is the universal gas constant (8.31452 J mol^{-1} K^{-1}). In chemistry, the aging activation energy is the minimum quantity of energy which the reacting components must possess to initiate the aging reactions.

To perform the kinetic analysis of bio-oil aging, the parameters of the aging kinetic model including the MW_∞ values for different aging temperatures and the aging kinetic parameters k_0 and E_a should be calculated. The traditional method for the estimation of the model parameters includes two separated fitting steps:

Step 1. Fitting Equation (2) to experimental data at each aging temperature and obtain k and MW_∞ values for each aging temperature;

Step 2. Fitting Equation (3) to resulting k_i *vs.* T_i (i = 1, …, n, where n is the number of aging temperatures considered) for different aging temperatures and obtain k_0 and E_a.

Obviously, the first fitting step leads to some errors involved in k_i as the bio-oil aging kinetic model (Equation (2)) is an empirical model and it cannot describe the aging kinetic behaviors of bio-oils without any deviation, and the experimental data contain some measurement errors. The errors contained in the resulting parameters (k_i) would be propagated when they will be used as the input data set in the second fitting step. The errors involved in the obtained aging kinetic parameters k_0 and E_a would be amplified.

4 Advanced procedure for aging kinetic analysis

To avoid the problem resulted from the traditional method, an alternative method is proposed in this study, which simultaneously considers the experimental data obtained at different aging temperatures.

Inserting Equation (3) in Equation (2) obtains the following equation:

$$\mathrm{MW}(t)=\mathrm{MW}_0+\left(\mathrm{MW}_\infty-\mathrm{MW}_0\right)\left\{1-\exp\left[-k_0\exp\left(-\frac{E_a}{R\cdot T_a}\right)\cdot t\right]\right\} \quad (4)$$

The above aging kinetic model describes the variation of weight-average molecular weight with the aging time and temperature.

The above model for bio-oil aging kinetics is applied simultaneously in order to adjust three MW – t curves at different aging temperatures. The estimation of the model parameter values and the investigation of the model quality are generally carried out by means of an objective function [39], which usually uses the sum of the squared errors between the experimental data and model prediction:

$$\mathrm{O.F.}\left(k_0, E_a, \mathrm{MW}_{\infty,1}, \mathrm{MW}_{\infty,2}, \ldots\right)=\sum_{j=1}^{n_i}\sum_{i=1}^{n_{i,d}}\left(\mathrm{MW}_{\exp,ij}-\mathrm{MW}_{\mathrm{cal},ij}\right)^2 \quad (5)$$

where MW_{exp} is the experimentally obtained weight-averaged molecular weight, MW_{cal} is the calculated weight-average molecular weight value obtained by numerical calculation of Equation (4) with the given set of parameters, and the subscript i denotes the i-th data point and the subscript j makes reference to a point in the j-th aging temperature. From Equation (5), the experimental data at all aging temperatures were considered in this study. When Equation (4) is solved using certain parameter values, the MW_{cal} and then O.F. values can be calculated. The aging kinetic parameter values can be obtained by minimizing the above objective function with some constraints:

$$\min_{p} \ \text{O.F.}\left(p\right) \quad \text{subject to: LB} \le p \le \text{UB} \qquad (6)$$

where p is the vector of parameters including MW_{∞} values at different aging temperatures, k_0 and E_a. LB and UB are lower and upper bound constraints for p, respectively.

If the experimental data set at only one aging temperature would be used, the aging kinetic parameters could be determined by using a common nonlinear fitting method. When the experimental data sets at all aging temperatures are considered, undeterminated parameters include $MW_{\infty,i}$ (i=1, …, n, where n is the aging temperatures considered in this study), k_0 and E_a, and the corresponding objective function may cause some difficulties in the use of the common nonlinear fitting method. In the present paper, the pattern search method is employed to solve the above optimization problem. The method, as an optimization method, does not require derivative information of the objective function [40]. The pattern search method is commonly used in science and engineering to generate high-quality solutions to optimize and search problems including parameter estimation of kinetic models because of its advantages in robustness and function evaluations [41, 42]. The detailed implementation of the pattern search method can found in the literature [43]. With each set of parameters, the objective function values associated with the old and new parameter sets are calculated. If the new parameter set reduces the function value, it is accepted for the next iterative calculation. **Figure 1** depicts the block diagram of this advanced procedure for bio-oil aging kinetic analysis.

Based on the above analyses, the advantages of the proposed advanced procedure for bio-oil aging kinetic analysis can be summarized as follows: (1) the developed comprehensive aging kinetic model considers the effect of both aging time and temperature on aging kinetics; (2) the experimental data at all aging temperatures are simultaneously used to perform the aging kinetic analysis; (3) the pattern search method is used to determine the aging kinetic parameters.

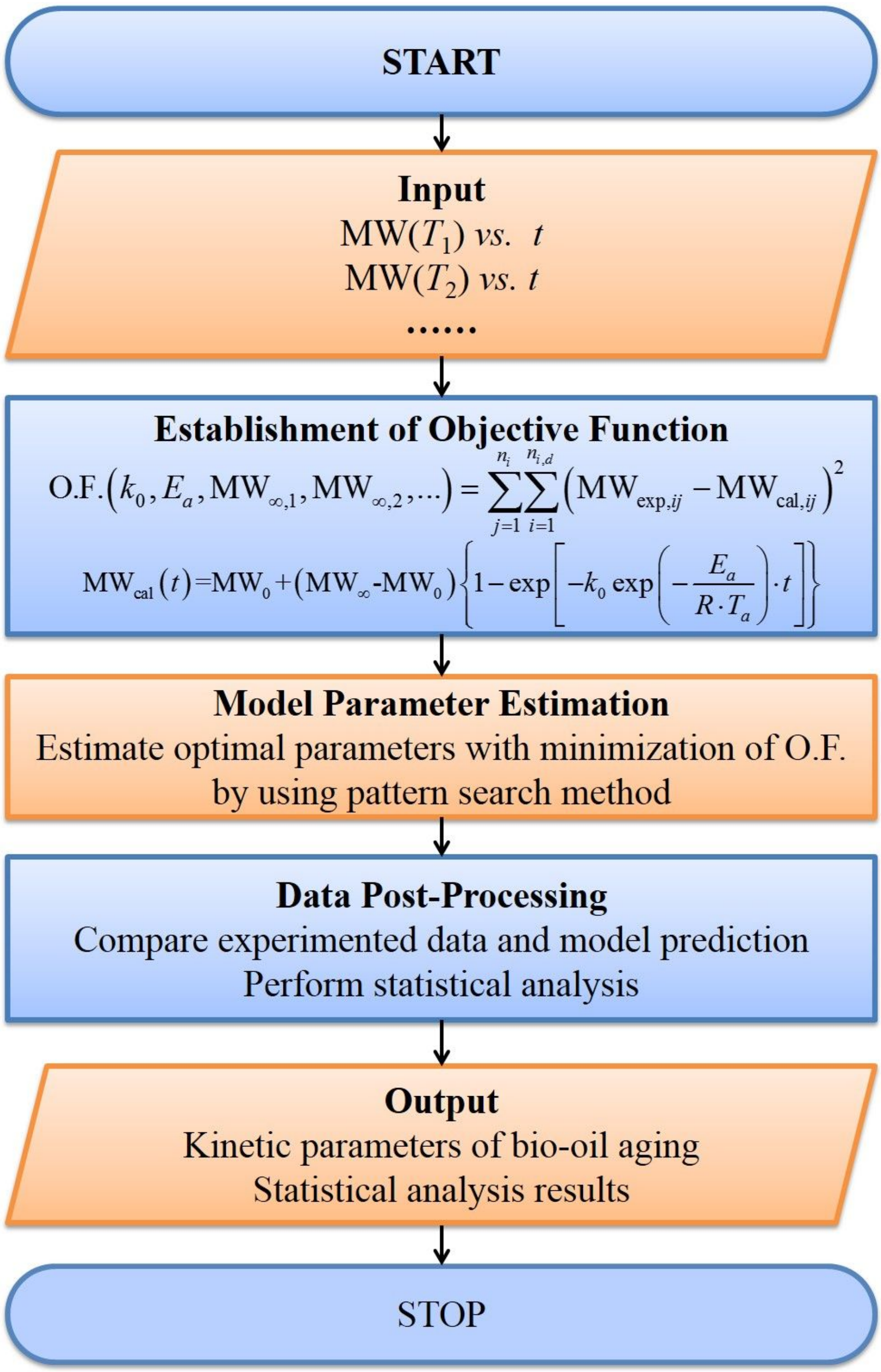


Figure 1. Block diagram of advanced procedure for bio-oil aging kinetic modeling

5 Results and discussion

5.1 Properties of fresh bio-oil

Table 1 lists the basic properties of bio-oil sample before aging. For comparison, the properties of heavy fuel oil [44] are also included in **Table 1**. From **Table 1**, it can be obtained that bio-oil contains much higher water content than heavy fuel oil and has a HHV of less than half of heavy fuel oil.

Table 1. Physicochemical properties of fresh bio-oil sample and heavy fuel oil

Property	Unit	Bio-oil	Heavy fuel oil [44]
Density	g mL^{-1}	1.26 ± 0.02	0.95
Water content	wt.%	12.1 ± 0.6	0.32
pH value		2.87 ± 0.01	
Dynamic viscosity @ 313 K	cP	95.3 ± 0.2	123.5
Higher heating value (HHV)	MJ kg^{-1}	17.43 ± 0.24	44.23
Weight-average molecular weight		532.5 ± 15.2	

5.2 Changes in water content and viscosity during aging

The water contents for all bio-oil samples increased slightly from 12.1 to 13.2 wt.% as the aging time and temperature increased. The slight increase of water content is caused by some condensation and dehydration reactions [45].

The changes in bio-oil's viscosity during aging at different temperatures of 303, 333 and 363 K are shown in **Figure 2**. The viscosity of bio-oils was found to gradually increased with aging time and higher aging temperatures favored the increase. This study mainly focused on the aging kinetic analysis on the change in average molecular weight. The viscosity-based kinetic modeling for bio-oil aging is not considered here and will be done in our future work.

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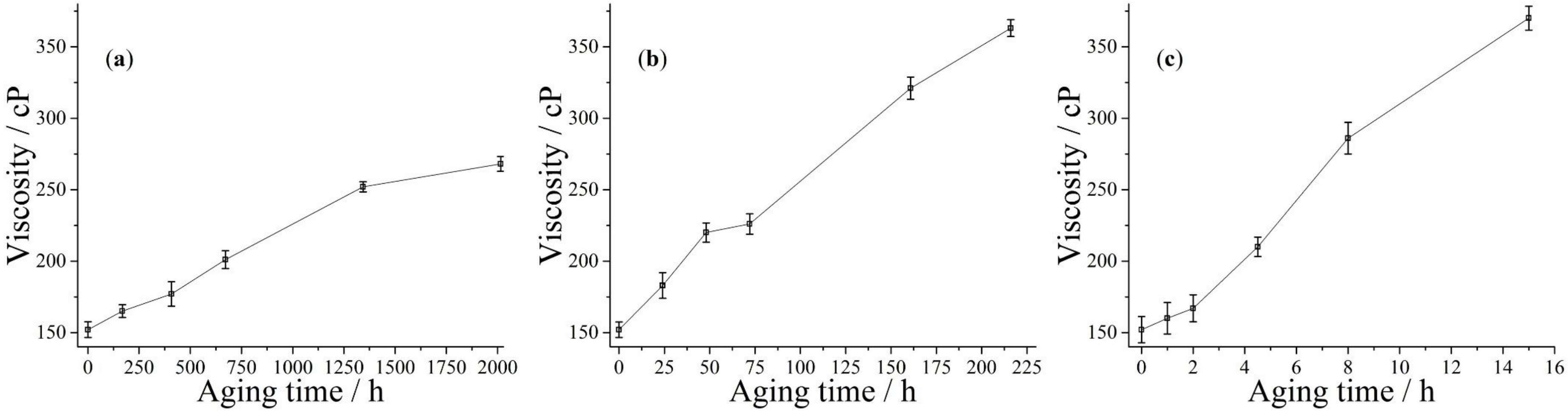

Figure 2. Changes in viscosity of bio-oil samples at aging temperatures of (a) 303 K, (b) 333 K, and (c) 363 K

5.3 Bio-oil aging kinetic analysis using traditional method

The traditional method of processing experimental kinetic data of bio-oil aging was conducted in this study. The fittings of the aging experimental kinetic data of the bio-oil sample at different temperatures with the kinetic model (2) were performed in DataFit (a powerful tool for nonlinear regression, statistical analysis, and data plotting) and the corresponding aging kinetic parameter values were obtained (as listed in **Table 2**).

Table 2. Aging kinetic parameter values at different aging temperatures from the traditional method

T_a / K	MW_∞	k / s^{-1}
303	856.4	4.8285×10^{-4}
333	954.3	9.0011×10^{-3}
363	1001.8	9.2882×10^{-2}

Based on the obtained k values at different aging temperatures, the E_a and k_0 values for the aging of the bio-oil sample can be calculated by using Equation (2): $E_a = 92.479$ kJ mol^{-1} and $k_0 = 28.400$ s^{-1}, respectively. The aging kinetic data were reproduced by using the aging kinetic model with the obtained parameter values and the comparison results between the experimental data and the reproduced curves for bio-oil aging at different temperatures are shown in **Figures 2, 3** and **4**. And the percentage root mean square error (PRMSE) was introduced as a quantitative statistical parameter. It is defined as follows [46]:

$$\text{PRMSE}=\frac{\sqrt{\frac{1}{n_d}\sum_{i=1}^{n_d}\left(\text{MW}_{\exp,i}-\text{MW}_{\text{cal},i}\right)^2}}{\overline{\text{MW}_{\exp}}}\times 100\% \qquad (7)$$

where $\overline{\text{MW}_{\exp}}$ is the average value of weight-average molecular weight during aging. The PRMSE values between the experimental data and the reproduced curves for bio-oil aging at different aging temperatures were listed in **Table 3**. From **Figures 3, 4, and 5** and **Table 3**, it can be easily noticed that there are relatively large deviations between the experimental data and the model predicted data.

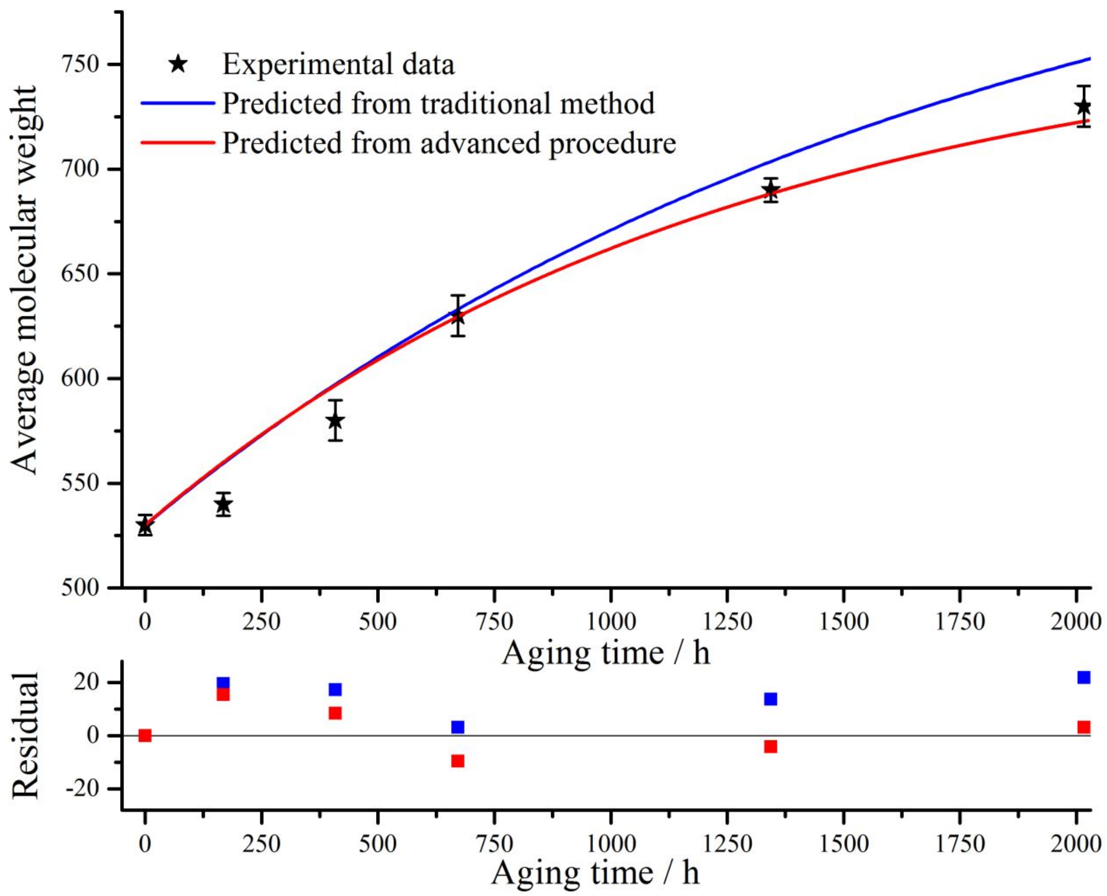

Figure 3. Comparison between experimental data and data predicted from the traditional method and advanced procedure for bio-oil aging kinetic analysis at the aging temperature of 303 K

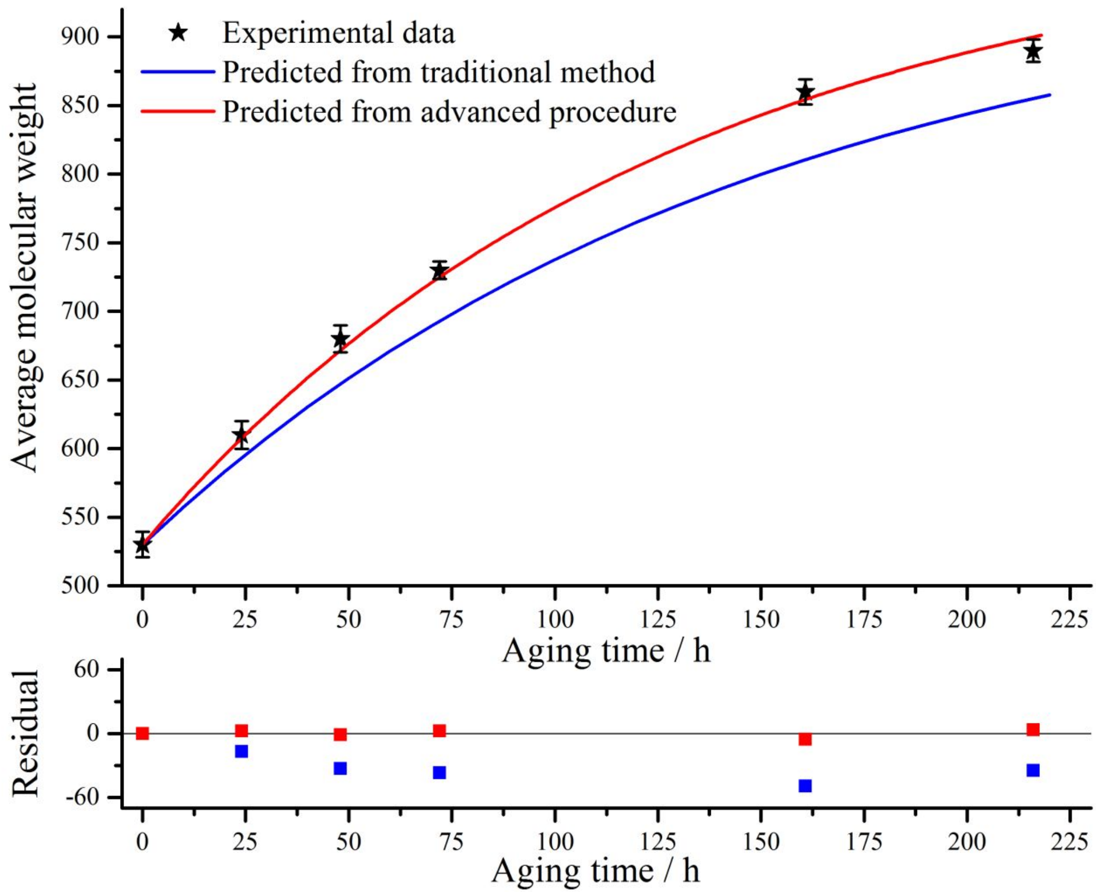

Figure 4. Comparison between experimental data and data predicted from the traditional method and advanced procedure for bio-oil aging kinetic analysis at the aging temperature of 333 K

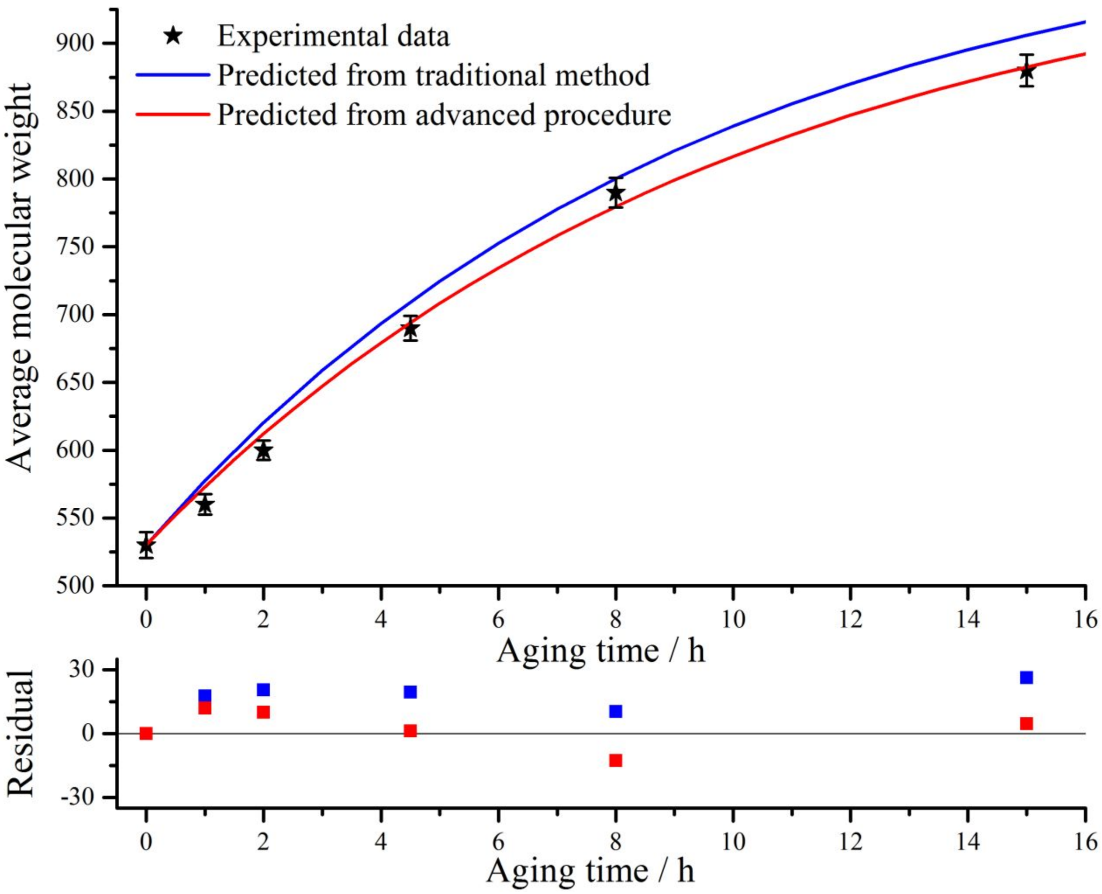

Figure 5. Comparison between experimental data and data predicted from the traditional method and advanced procedure for bio-oil aging kinetic analysis at the aging temperature of 363 K

Table 3. Aging kinetic parameters for bio-oil aging and corresponding statistical analysis results

Method	k_0 / s^{-1}	E_a / kJ mol^{-1}	PRMSE		
			@303K	@333K	@363K
Traditional method	28.400	92.478	4.87%	9.11%	5.27%
Advanced procedure	25.990	85.446	1.37%	0.43%	1.24%

5.4 Bio-oil aging kinetic analysis using advanced procedure

In order to investigate the effect of k_0 and E_a values on the objective function (5), the change of O.F. values calculated for different k_0 and E_a values (k_0 = 12 – 32 s^{-1} step 0.01 s^{-1}, E_a = 74 – 94 kJ mol^{-1} step 0.01 kJ mol^{-1}) and given MW_∞ values is shown in **Figure 6**. As it can be obviously observed in **Figure 6**, the O.F. 3-D scatter plot shows that there are a certain minimum value and is different for different given MW_∞ values. In **Figure 6**, the red 3-D ball represents the minimum point for each set of MW_∞ values. Considering the results of above analysis and the complexity of the optimization problem (6), a certain advanced optimization method needs to be taken into account.

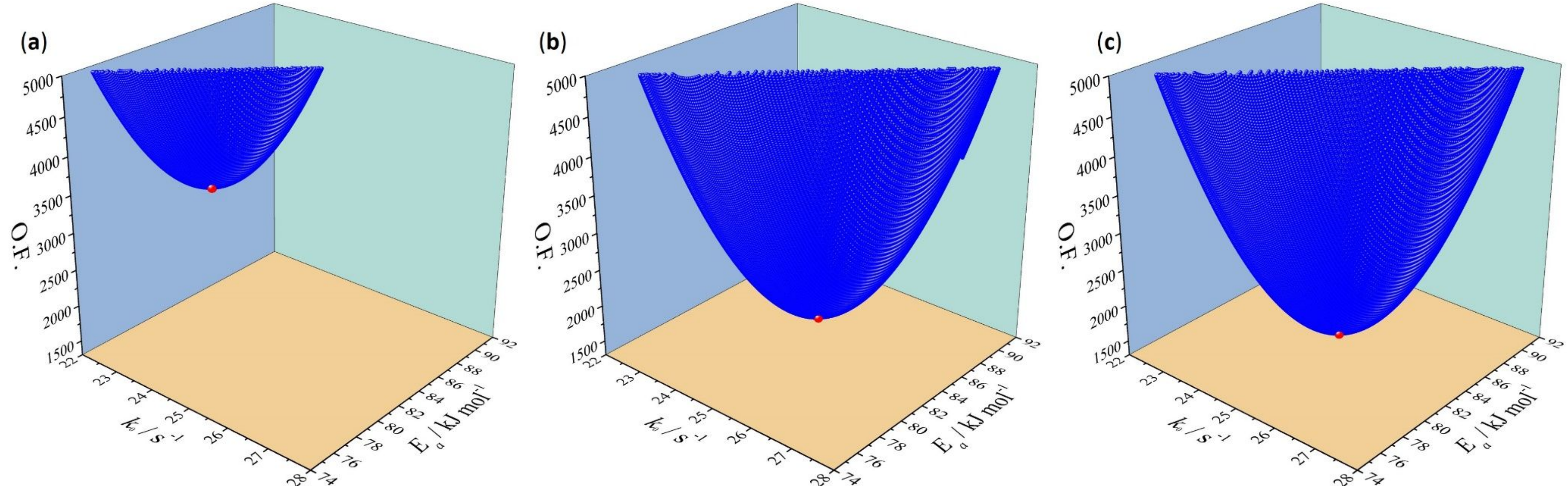

Figure 6. Changing of O.F. depending on different k_0 and E_a values with given MW_∞ values: (a) $MW_{\infty,1} = 755$, $MW_{\infty,2} = 1055$, $MW_{\infty,3} = 1085$; (b) $MW_{\infty,1} = 760$, $MW_{\infty,2} = 960$, $MW_{\infty,3} = 990$; (c) $MW_{\infty,1} = 755$, $MW_{\infty,2} = 1055$, $MW_{\infty,3} = 1085$.

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As mentioned above, the pattern search method is considered in this study, which is implemented in the MATLAB software environment. In the beginning of the implementation of the pattern search method, an initial guess of the aging model parameters should be given. In this study, the minimum point in **Figure 6(c)** is chosen as the initial guess for the optimization. **Figure 7** shows the best objective function value at every iteration, function evaluation numbers per interval and mesh size at every iteration. The results included in **Figure 7** indicate that the objective function decreases with iteration. Initially it sharply decreases, then level off.

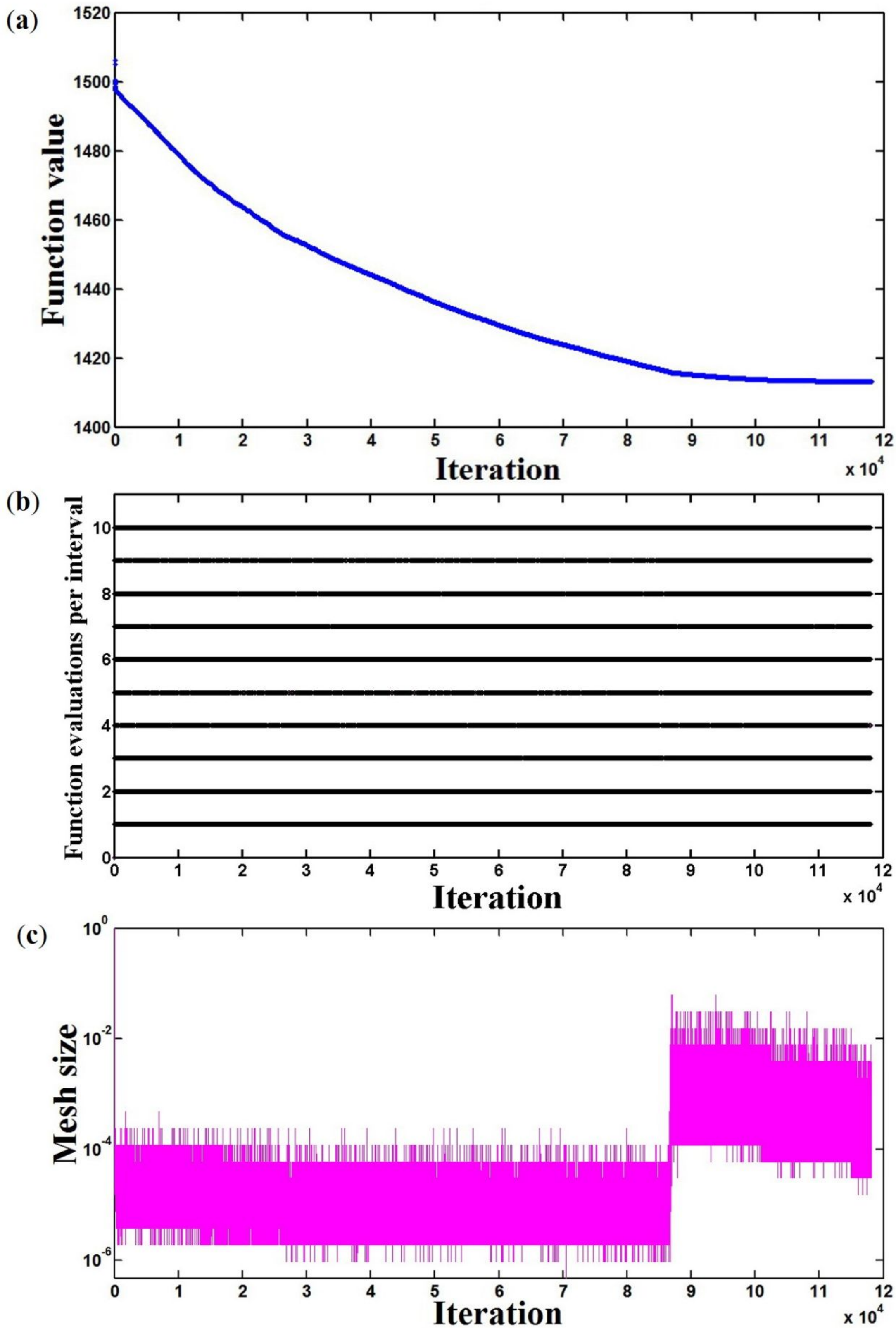

Figure 7. (a) Best objective function value at each iteration; (b) Function evaluations per interval; (c) Mesh size at each iteration for optimization calculation using pattern search method

The optimized aging kinetic parameters are established by the advanced procedure and listed in **Table 3**. The comparison of predicted aging kinetic curves with the above optimized parameters with the experimental data are also shown in **Figures 3, 4, and 5** for aging temperatures of 303, 333 and 363 K, respectively. The corresponding PRMSE values between the experimental data and model prediction are listed in **Table 3**. The results included in **Figures 3**, **4**, and **5** and **Table 3** demonstrate that the aging kinetic model (4) can fit the aging experimental data of the bio-oil sample sufficiently well for all aging temperatures.

To evaluate the validity of the comprehensive aging kinetic model, the experimental data point at aging temperature of 363 K and aging time of 24 h and the experimental data set at aging temperature of 353 K with aging time ranging from 0 to 60 h, which were not used for the calculation of the aging kinetic parameters, were compared with the data from the aging kinetic model with the optimized kinetic parameter. From **Figure 8**, the model prediction describes the experimental data well. This indicated that the developed model and the obtained kinetic parameters were effective for describing the aging kinetic behaviors of the bio-oil samples.

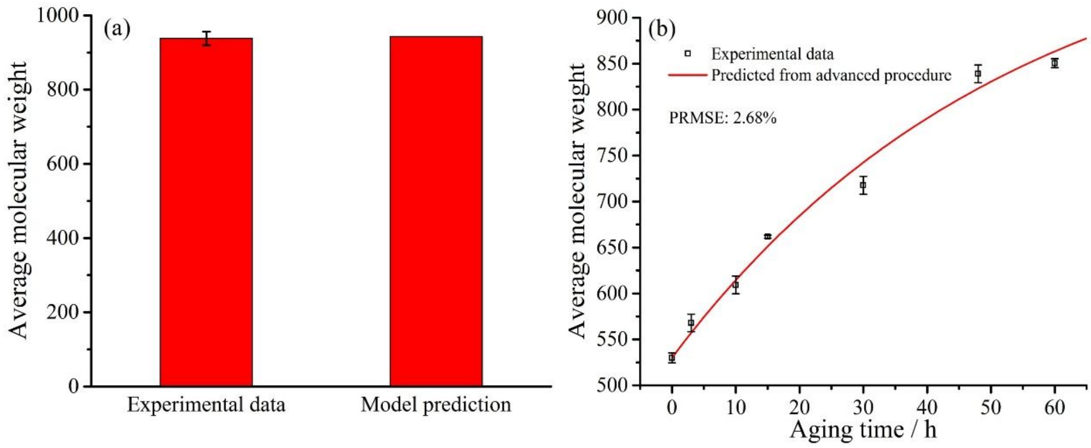

Figure 8. Verification of the model prediction usability for bio-oil aging at (a) aging temperature: 363 K, aging time: 24 h; (b) aging temperature: 353 K, aging time: from 0 to 60 h.

The aging kinetic behaviors at interpolated and extrapolated aging temperatures can be predicted by means of the numerical calculations of the aging kinetic model (4) with the optimized aging kinetic parameters. In addition, differentiating the aging kinetic model (4) with respect to *t*, the change rate of weight-average molecular weight with the aging time can be obtained (see Equation (8)).

$$\frac{\mathrm{dMW}}{\mathrm{d}t}(t) = k_0\left(\mathrm{MW}_\infty - \mathrm{MW}_0\right)\exp\left[-\frac{E_a}{R\cdot T_a} - k_0\exp\left(-\frac{E_a}{R\cdot T_a}\right)\cdot t\right] \qquad (8)$$

Figure 9 shows the predicted curves of the change and change rate of weight-average molecular weight with the aging time at the interpolated and extrapolated temperatures of 313, 323, 348 and 368 K. From **Figure 9**, it can be obtained that (1) the weight-average molecular weight of the bio-oil sample increases with the aging period, (2) the change and change rate of weight-average molecular weight are greater at higher temperatures (e.g., 348 and 368 K) than those occur at lower temperatures (e.g., 313 and 323 K). The results included in **Figure 9** reveal that weight-average molecular weight of the bio-oil sample after 60 days of aging at 313 K is equivalent to that obtained after approximately 278 hours at 323 K, to 27.3 hours at 348 K and to 5.3 hours at 368 K.

The weight-average molecular weight of bio-oils significantly increased with increasing aging time, that indicates the formation of large molecules. And higher temperatures favor the increase of average molecular weight. The results are in good agreement with the widely accepted bio-oil aging mechanism that refers the bio-oil aging is mainly caused by self-condensation reactions and some mutual interactions of different bio-oil fractions [18, 47]. Those condensation reactions accelerate greatly with increasing aging temperature [48].

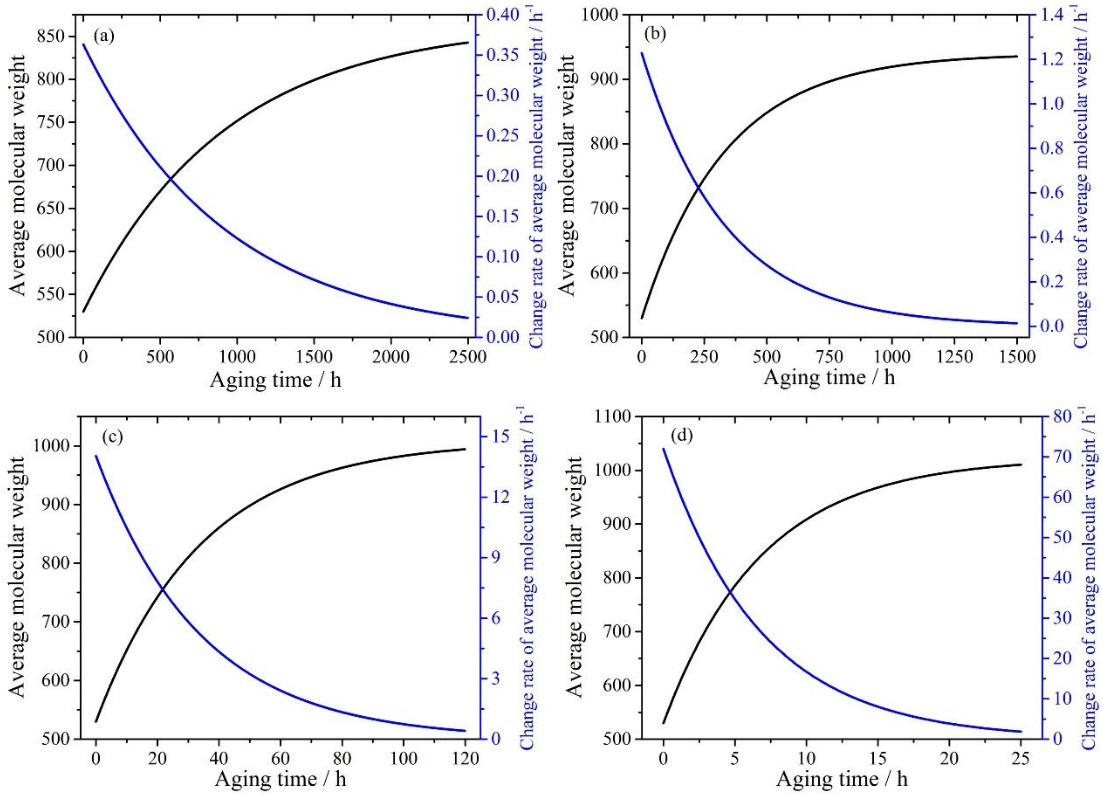

Figure 9. Aging kinetic behaviors at aging temperatures of (a) 313 K, (b) 323 K, (c) 348 K and (d) 368 K predicted from comprehensive aging kinetic model with optimized kinetic parameters

6 Conclusions

This study focuses on the investigation of bio-oil aging characteristics in terms of change in weight-average molecular weight and performing kinetic modeling of bio-oil aging. The advanced procedure based on the pattern search method has been developed to accurately analyze the kinetic experimental data of bio-oil aging. The following findings and conclusions are drawn: (1) The aging kinetic experiments of the bio-oil sample from poplar wood pyrolysis at different aging temperatures are performed. The change and change rate in the weight-average molecular weight of bio-oil are greater at higher temperatures than those occur at lower temperatures. (2) The aging kinetic analysis based on the traditional method with two separated fittings can't provide accurate results. (3) The advanced procedure to process kinetic experimental data of bio-oil aging has been developed by simultaneously considering all aging temperatures and using the pattern search method. The results predicted from the comprehensive aging kinetic model coupled with the optimized kinetic parameters were compared with the aging kinetic experimental data of bio-oil at different temperatures. The aging kinetic model with the optimized parameters obtained from the advanced procedure describes the experimental data at different temperatures more reliable and accurate than that from the traditional method.

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