Study on Evaporation Characteristics of Bio-oil and its Compound Models

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In this study, bio-oil was analyzed by gas chromatography mass spectrometry (GC-MS), and the evaporation characteristics of bio-oil were studied at different heating rates (10, 20, and 30 °C/min) from 35 °C to 250 °C by a thermal analyzer (TG-DSC). The TG-DSC results of bio-oil showed that the heat requirement of bio-oil during the evaporation process ranged from 2.072×10^3 to 2.299×10^3 J/g, and the bio-oil activation energy ranged from 1.22×10^4 to 3.34×10^4 J/mol. Moreover, four models with five compounds (methanol, water, ethanol, furfural, and phenol) were established to study the bio-oil evaporation process. By comparing the TG-DSC results of bio-oil and its models at 30 °C/min, it was shown that the optimal model was model 2, which has the following chemical composition: methanol (27.10 wt.%), water (44.96 wt.%), ethanol (16.24 wt.%), furfural (4.40 wt.%), and phenol (7.30 wt.%). Model 2 exhibited a minimal relative error in dynamic parameters and characteristic curve parameters. The errors for activation energy of the TG, activation energy of the DSC, maximum endothermic rates, and the total of the heat absorption were 3.04%, 5.88%, 2.49%, and 1.06%, respectively.

Keywords: GC-MS; TG-DSC; Model compound; Bio-oil

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INTRODUCTION

Bio-oil from fast pyrolysis of biomass, owing to its eco-friendly properties, is currently regarded as a potential renewable liquid fuel arising from a maturing technology (Mohan *et al*. 2006; Ragauskas *et al*. 2006). There are more than 400 types of chemical components contained within this fuel, including large amounts of water, acids, alcohols, aldehydes, ketones, phenols, ethers, esters, furans, and other organics (Demirbas 2007; Kunkes *et al*. 2008; Zhang *et al*. 2007). Many complex chemical reactions can occur with the various components. It is these reactions which limits this study from elucidating the reaction mechanism for the biofuel.

As a result of the limitation of the research duration and cost, it is difficult to explore the mechanism in the application process of bio-oil. In replacement of bio-oil, model compounds became one of the important means to study the application mechanism. Vagia and Lemonidou (2007) selected acetic acid and oxalic acid instead of bio-oil to study the process of the hydrogen production by steam reforming of bio-oil and the dynamic mechanism in the process. Xie *et al.* (2011) successfully demonstrated the validity of using methanol, acetic acid, and ethylene glycol as model compounds for hydrogen production from bio-oil. Adjaye and Bakhshi (1995) successfully simulated the catalytic cleavage reaction of bio-oil using nine kinds of organics. Senol *et al*. (2005)

studied the catalytic hydrogenation mechanism with the model compounds methyl hexanoate and methyl heptanoate using the catalysts in a flow reactor to discern the reaction schemes.

These model compounds were chosen mainly based on chemical properties of bio-oil. They were suitable to study the mechanisms in hydrodeoxygenation and catalytic cracking of bio-oil, but inadequate to study the mechanisms in gasification, combustion, and evaporation of bio-oil due to the presence of the heat and mass transfer in these processes. To study the latter mechanisms, along with the composition of bio-oil, it is necessary to consider the boiling point, latent heat, thermal conductivity, and other thermodynamic properties of each component.

Recently, it was widely reported that thermal analysis was utilized to study the characteristics of gasification, combustion, and evaporation. Ambalae *et al*. (2006) used a thermogravimetric analyzer to study the pyrolysis and combustion behavior of both crude oil and its asphaltenes. Herod *et al*. (2007) used thermal analysis to study oil distillation, and the distribution of heavy oil boiling point was obtained. Some investigators (Pieterse and Focke 2003; Viswanathan *et al*. 2009) measured the vapor pressure of volatile substances with thermal analysis. In addition, applying the thermal analysis to the reaction kinetics was also gaining extensive attention. Chen *et al.* (2012) studied the drying kinetic of biomass using a thermal analyzer (TG-DSC). Hazra *et al.* (2004) studied the kinetics of oil evaporation and found that the evaporation process could be fitted with the Arrhenius equation. The TG-DSC approach, however, has not been widely used for evaporating research of bio-oil. Thereafter, further development of the TG-DSC approach will be required to provide mass and heat transfer characteristics in the evaporation process of bio-oil.

Therefore, this study aimed to achieve the following goals. The evaporation characteristics were investigated using the TG-DSC method, and in conjunction with gas chromatography-mass spectroscopy (GC-MS) a novel method developed to establish compound models for simulating the evaporation process of bio-oil. The optimal compound model was also developed by comparing the TG-DSC results of bio-oil and the proposed models. The best compound model provides a theoretical basis to study the heat and mass transfer of bio-oil and the evaporation mechanism of the pyrolysis gas chromatography.

EXPERIMENTAL

Materials

The bio-oil used in this experiment was produced from rice husk at a fast pyrolysis pilot plant located in Hefei, China. The reagents used in this study were all analytically pure (Sinopharm Chemical Reagent CO., Ltd, China), and all water was distilled.

Methods

GC-MS method

The chemical composition was analyzed by GC-MS (Trace DSQ II; Thermo Scientific, USA) equipped with a TR-5MS capillary column (30m×0.25mm×0.25 μm). The oven temperature was controlled as follows: an initial temperature of 40 °C was maintained for 3 min, and then gradually heated to 180 °C during a period of 35 min, after which the oven was heated to a final temperature of 280 °C within a 10 min interval and subsequently maintained at that temperature for another 4 min.

TG-DSC method

The TG-DSC experiments were analyzed by a thermal analyzer (SDT Q600, TA Instruments Co., USA). This instrument was specifically designed to support both thermogravimetry (TG) and differential scanning calorimetry (DSC) measurements. The measuring precision of weight and temperature was 0.1 μg and 0.001 °C, respectively. The calorimetric accuracy of DSC was ±2%. In each experiment, the carrier gas was N_2, and the flow rate was kept at 100 mL/min. The thermal analyzer heated the sample at different heating rates (10, 20, and 30 °C /min) from 35 °C to 250 °C.

RESULTS AND DISCUSSION

GC-MS Analysis of Bio-oil

Analysis of the GC-MS data reveals a complexity of compounds present in bio-oil. Table 1 lists the compounds with a relative peak area greater than 0.5%.

Table 1. Main Chemical Compounds of Bio-oil

NO.	Compound	RT (min)	Relative content (%)
01	Methanol	1.75	8.56
02	Acetate	2.06	1.77
03	Acetic acid	4.17	8.26
04	1-Penten-3-ol	6.39	1.82
05	Furfural	7.66	5.20
06	3-Methoxy-1-propene	8.85	3.23
07	2,5-Dimethylfuran	10.09	0.89
08	2-Hexene	11.13	0.80
09	Phenol	13.44	4.21
10	2 – Methylphenol	16.13	1.87
11	2-Methoxyphenol	17.21	3.44
12	2,3-Dimethylphenol	19.49	1.12
13	4- Methyl-2-methoxyphenol	20.94	2.40
14	1,2-Benzenediol	21.50	0.91
15	1,4-Benzenediol	21.67	0.81
16	5-Ethyl-2-methylphenol	22.18	0.57
17	2,4-Dimethoxytoluene	23.82	1.51
18	4-Propenyl-2-methoxyphenol	26.47	1.60

TG-DSC Analysis of Bio-oil

Characteristic parameter analysis

The results of the bio-oil thermogravimetry experiments are illustrated in Fig. 1, which suggests high similarity of the characteristics and trends of curves at different heating rates. As shown in Figs. 1b and 1c, when the temperature increases, both DTG values and heat flow reach peaks at the first inflection point (denoted by X and Y, respectively), but then drop sharply to very low levels. Therefore, the evaporation process of bio-oil can be divided into two stages. The interval of the DTG decrease to the first inflection point after the peak is the first stage, and the interval above the inflection point to the end is the second stage. In the first stage, low boiling point compounds (such as methanol, water, and acetic acid) evaporate first, which leads to a weight loss of more than 75%. In the second stage, larger molecular components (such as phenol, vanilline, and saccharide) decomposed, and the char, tar, and gas were produced. Moreover, the DTG and heat flow of the second stage were almost a constant value, and the weight loss in the second stage was much less than in the first stage. Therefore, it was not necessary to analyze the second stage, and the first stage was selected for further analyses in this study.

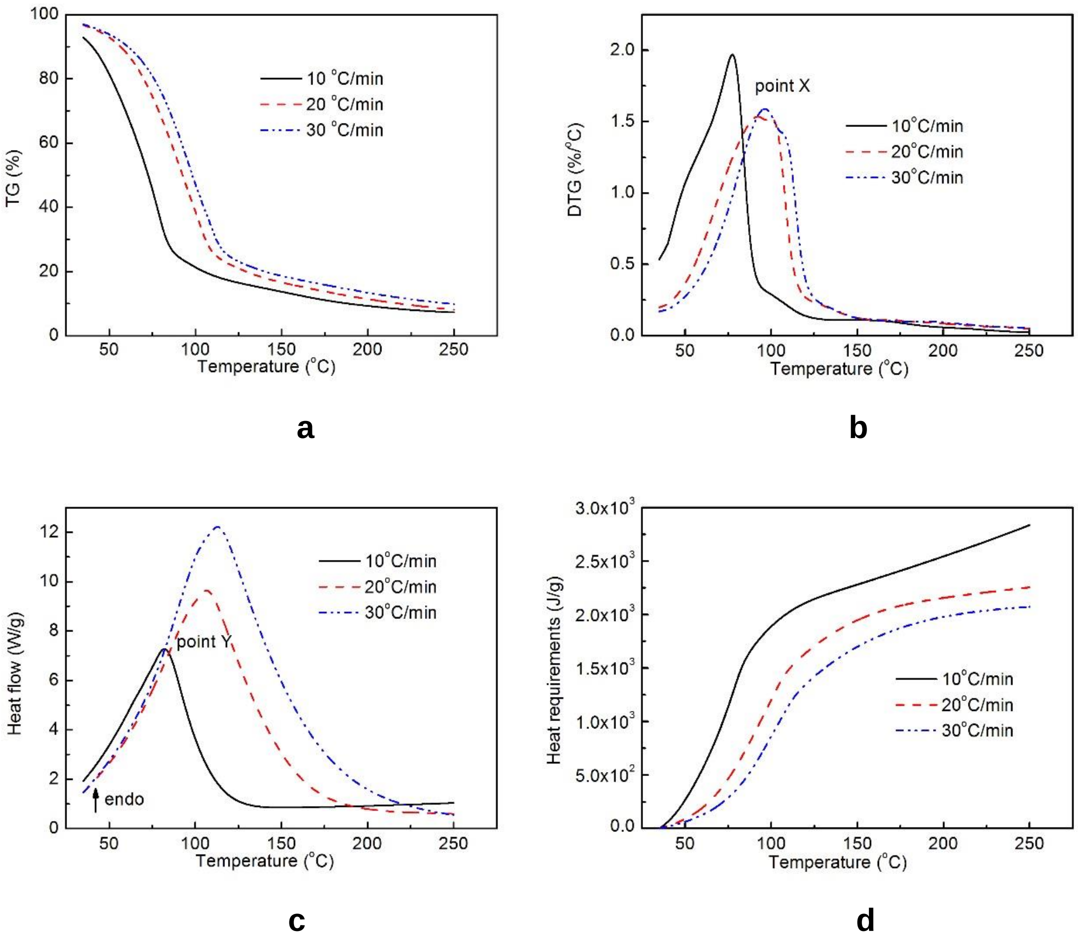


Fig. 1. (a) TG, (b) DTC, (c) DSC, and (d) heat requirement curves of bio-oil at 10, 20, and 30 °C/min in N_2 atmosphere

Besides the points X and Y, the peak area of the DSC curves is a valuable indicator of total heat absorbed by bio-oil. Therefore, this study uses the value of X, Y, and total heat as characteristics of bio-oil TG-DSC curves. These results are shown in Table 2.

Table 2. Characteristic of Bio-oil TG-DSC Curves

Heading rate (°C/min)	Point X		Point Y		Total heat (J/g)
	Temperature (°C)	DTG (%/°C)	Temperature (°C)	Heat Flow (W/g)	
10	77.53	1.969	81.79	7.272	2.299×10^3
20	92.52	1.535	106.29	9.642	2.178×10^3
30	96.17	1.590	112.76	12.220	2.072×10^3

As seen in Table 2, at the same heating rate, the temperature corresponding to maximum heat flow (point Y) is higher than the temperature corresponding to maximum weight loss (point X). This suggests that there were some differences between the thermal and quantity alterations of bio-oil during experiments. The reason was that the response rate of the heat transfer was slower than that of the mass transfer. When the experimental curves were compared under different heating rates, the results showed that peak temperatures of the TG-DSC curves were elevated when the heating rate increased. Based on the results from Fig. 1 and Table 2, it is possible to conclude that the influence of the heating rates is more substantial on the heat absorption rate than on the rate of weight loss. The higher the heating rate value, the larger the heat absorption rate.

Kinetic analysis

This paper uses the Arrhenius correction equation to analyze kinetic characteristics of the bio-oil evaporation process (Fu *et al*. 2006):

$$\frac{d\alpha}{d\tau} = A(T+273.15)^k \exp\left(-\frac{E}{R(T+273.15)}\right) \tag{1}$$

where τ is the reaction time (s), A is the frequency factor, E is the evaporation activation energy of bio-oil (J/mol), R is the gas constant (R=8.314 J/(K·mol)), T is the thermodynamic temperature (°C), and k is the reaction series, where k in this experiment is -2.

The parameter α is determined by the type of curves. In the analysis of the TG curves, the following equation is used:

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \tag{2}$$

where m_0 is the initial quantity of bio-oil (g), m is the quantity of bio-oil for moment (g), and m_∞ is the final quantity of bio-oil (g). For analysis of the heat absorption curves, the following formula is used:

$$\alpha = \frac{H}{H_\infty} \tag{3}$$

where H is the absorption heat at time (τ) (J/g), and H_∞ is the total absorption heat of bio-oil (J/g) (Zhao *et al*. 2012). Replacing the heating rate, which is defined as $\beta = \frac{\mathrm{d}T}{\mathrm{d}\tau}$, into Eq. 1, and integrating, yields:

$$\alpha = \frac{AR}{\beta E}\exp\left(-\frac{E}{R(T+273.15)}\right) - C \tag{4}$$

Eq. 4 is used to fit the TG-DSC data of bio-oil. The results are shown in Table 3.

Table 3. Results of the Kinetic Analysis of Bio-oil

	β (°C/min)	Temperature range (°C)	*E* (J/mol)	*A*	*C*	R^2
Kinetic analysis of TG	10	35-97	1.22×10^4	1.25×10^6	0.71	0.987
	20	35-112	2.84×10^4	4.87×10^8	0.11	0.994
	30	35-118	3.13×10^4	1.67×10^9	0.07	0.992
Kinetic analysis of DSC	10	35-97	1.61×10^4	4.09×10^6	0.43	0.992
	20	35-112	2.88×10^4	4.63×10^8	0.11	0.996
	30	35-118	3.34×10^4	2.63×10^9	0.06	0.996

The coefficients of determination (R^2) are higher than 0.98, so it is accurate to use the proposed kinetic model to describe the bio-oil evaporation process (Table 3). Upon comparison of the activation energy between TG curves and DSC curves, the activation energy values obtained in both curves were very similar.

Establishment of Compound Models of Bio-oil

In accordance with the product distribution results (Table 1), five compounds were selected, including four organic species (methanol, acetic acid, furfural, and phenol), which were representative compounds with enriched presence in bio-oil; these compounds in addition to the inorganic compound water were used to establish the bio-oil model system. Many investigators selected some of these compounds to replace bio-oil in their research (Brett *et al*. 2010; Graca *et al*. 2009; Ye *et al*. 2012). The boiling points and latent values of these compounds are listed in Table 5, and relative amounts of these five compounds were determined by TG-DSC using the following methods:

In the first step, the TG and heat requirement curves of bio-oil were divided into five sections. These sections correspond to methanol, water, acetic acid, furfural, and phenol, which were sorted in increasing order of boiling point. The TG and heat requirement curves were divided into five sections by the following two methods: (1) The curves were divided according to the boiling point of the five components, namely 35~64.7 °C, 64.7~100 °C, 100~118.1 °C, 118.1~161.7 °C, and 161.7~181.9 °C; (2) The curves were divided according to the average boiling point of the adjacent components, namely 35~82.3 °C, 82.3~109.1 °C, 109.1~139.9 °C, 139.9~171.8 °C, and 171.8~250 °C.

In the second step, the relative content of the five compounds was determined by the following two calculations:

Calculation one is: $$w_i = \frac{\Delta m_i}{\sum_{i=1}^{5} \Delta m_i}.$$

Calculation two is: $$w_i = \frac{H_i / h_i}{\sum_{i=1}^{5} (H_i / h_i)}.$$

The value of the subscript *i* is from 1 to 5, and it denotes methanol, water, acetic acid, furfural, and phenol, respectively; w_i is the amount of the compound *i* (%); Δm_i is the weight loss of the chemical compound *i*, which is obtained by analyzing TG curves of bio-oil (Fig. 1a) (%); H_i is the absorbed heat of section *i*, which is obtained by analyzing the heat absorption curves of bio-oil (Fig. 1c) (J/g); and h_i is the latent heat of the compound *i* (J/g).

In this study, four component models were established from the TG curves and heat absorption curves of bio-oil at 30 °C/min by the orthogonal method (Keppel 1991). The models are defined in Table 4, and the content of each model is specified in Table 5.

Table 4. Method of Establishing the Component Models

	First step (dividing the curves)	Second step (calculating the relative content)
Model 1	Method One	Calculation one
Model 2	Method Two	Calculation one
Model 3	Method One	Calculation two
Model 4	Method Two	Calculation two

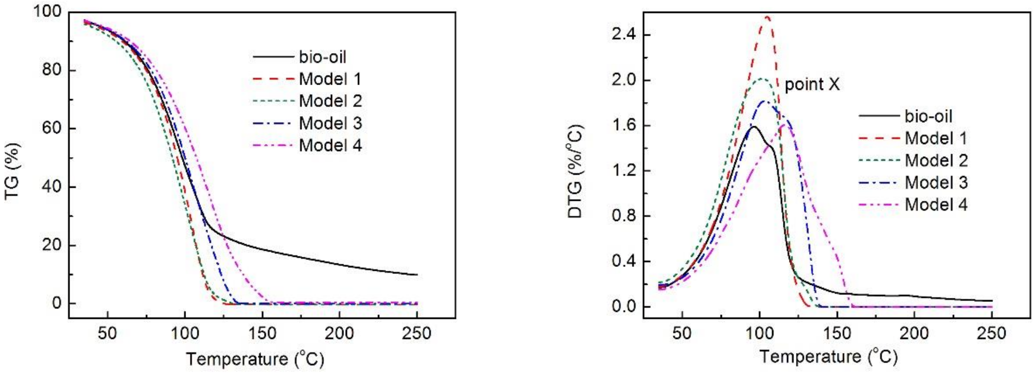
Table 5. Properties and Component Composition in Bio-oil

Compound	Boiling point (°C)	Latent heat (J/g)	Content of compound models (wt.%)			
			Model 1	Model 2	Model 3	Model 4
Methanol	64.7	1.10×10^3	10.72	27.10	5.21	12.77
Water	100.0	2.26×10^3	50.09	44.96	10.61	10.74
Acetic acid	118.1	3.95×10^2	26.71	16.24	39.30	41.70
Furfural	161.7	4.45×10^2	9.94	4.40	36.63	19.61
Phenol	181.9	4.85×10^2	2.54	7.30	8.25	15.18

Comparison of Compound Models to Bio-oil

The TG-DSC experiments are performed to test the above four models at a heating rate of 30 °C/min in a N_2 atmosphere. The results of the comparison between the models and bio-oil are shown in Fig. 2 and Fig. 3. A close inspection of Fig. 2 and Fig. 3 show that the variation trend of the curves of four models is similar to that of bio-oil. In this paper, the fitting effect of the compound models to bio-oil is discussed by analyzing the TG curves and DSC curves.

TG analysis



a **b**

Fig. 2. (a) TG and (b) DTG curves of bio-oil and four models at 30 °C/min in an N_2 atmosphere

As seen in Fig. 2, the agreement between the compound models and bio-oil is better at low temperatures than at high temperatures. This is because there is 10 wt.% left for bio-oil, but none is remaining when any model is tested. In order to directly compare the TG-DTG curves between the model compounds and bio-oil, the parameters are listed in Table 6.

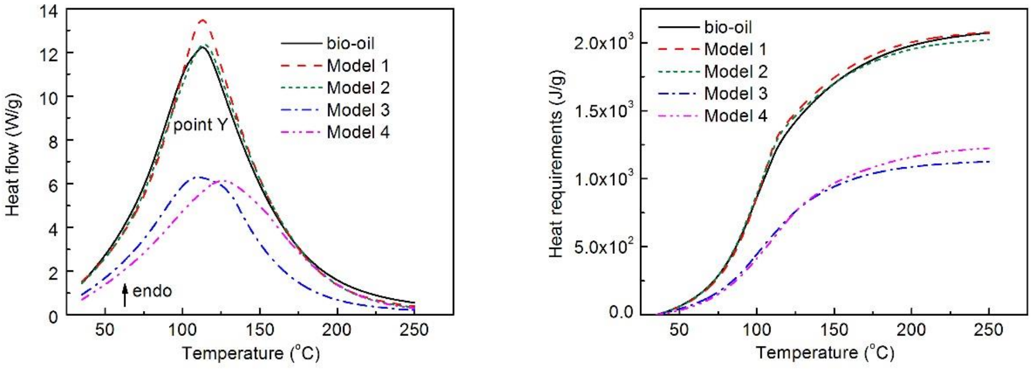
Table 6. TG Characteristics of Model Compounds and Bio-oil at 30 °C/min

		Bio-oil	Model 1	Model 2	Model 3	Model 4
Point X	Temperature (°C)	96.17	104.67	102.64	103.37	116.41
	DTG (%/°C)	1.59	2.56	2.01	1.82	1.60
	DTG *error** (%)	-	60.98	26.49	14.29	0.94
Kinetic analysis of TG	Temperature (°C)	35-118	35-120	35-119	35-135	35-118
	E (J/mol)	3.13×10^4	3.94×10^4	3.22×10^4	2.72×10^4	2.94×10^4
	*E error** (%)	-	25.92	3.04	13.03	5.85
	A	2.86×10^{10}	2.62×10^9	3.66×10^8	6.32×10^8	2.86×10^{10}
	C	0.029	0.066	0.100	0.056	0.029
	R^2	0.992	0.993	0.989	0.995	0.992

*Error corresponds to the relative error between the compound models and bio-oil

By comparing the peaks of TG-DTG curves between the model compounds and bio-oil, it was shown that the temperature of model 2 was the closest to the temperature of bio-oil, while the relative error of model 4 and bio-oil on the DTG curves peak value was minimal. The ascending order of the activation energy error of TG-DTG curves was model 2, model 1, model 3, and model 4. Moreover, since decomposing reactions occurred at high temperatures in bio-oil, the error of TG curves was large. Overall, TG-DTG curves of model 2 fit best to those of bio-oil. Therefore, it can be concluded that model 2 can replicate the mass transfer characteristics in the evaporation process of bio-oil with the best accuracy among these models tested.

DSC analysis



a **b**

Fig. 3. (a) The heat flow and (b) heat requirement curves of the bio-oil and the four models at 30 °C/min in an N_2 atmosphere

From Fig. 3, the curves of model 1 and model 2 almost coincide with the curves of bio-oil, while the curves of model 3 and model 4 have a large deviation from bio-oil. In order to make direct comparisons of the DSC curves between the model compounds and bio-oil, the parameters are listed in Table 7.

Table 7. DSC Characteristics of Model Compounds and Bio-oil at 30 °C/min

		Bio-oil	Model 1	Model 2	Model 3	Model 4
Point Y	Temperature (°C)	112.76	112.49	113.98	110.2	126.3
	Heat flow(W/g)	12.22	13.45	12.35	6.286	6.126
	Heat flow *error** (%)	-	10.15	1.06	48.56	49.87
Total heat (J/g)		2.07×10^3	2.13×10^3	2.02×10^3	1.13×10^3	1.22×10^3
Total heat *error** (%)		-	2.63	2.49	45.65	40.94
Kinetic analysis of DSC	Temperature (°C)	35-118	35-120	35-119	35-135	35-118
	E (J/mol)	3.34×10^4	3.75×10^4	3.54×10^4	2.25×10^4	2.49×10^4
	E *error** (%)	-	12.19	5.88	32.73	25.39
	A	2.63×10^9	1.07×10^{10}	4.22×10^9	5.84×10^7	1.21×10^8
	C	0.059	0.045	0.059	0.133	0.102
	R^2	0.996	0.994	0.995	0.993	0.994
*error corresponds to the relative error between the compound models and bio-oil						

As can be seen from the Table 7 and Fig. 3, with the exception of model 4, the peak temperatures of the component models are close to that of bio-oil. The relative error of the DSC curves peak value in ascending order is model 2, model 1, model 3, and model 4. The total heat error of model 1 and model 2 is less than 3%. Moreover, the relative error between model 2 and bio-oil is minimal at 5.88%. Therefore, the DSC curves of model 2 fit to the DSC curves of bio-oil best, and model 2 can truly reflect the heat transfer characteristics in the evaporation process of bio-oil.

In summary, by analyzing the TG-DSC curves of component models and bio-oil, it was shown that model 2 closely reproduces both mass transfer characteristics and heat transfer characteristics during the evaporation process of bio-oil. The errors were 3.04%, 5.88%, 2.49%, and 1.06% for activation energy of TG, activation energy of DSC, maximum endothermic rates, and the total of the heat absorption, respectively.

CONCLUSIONS

1. Evaporation characteristics of bio-oil were studied using a TG-DSC analyzer at different heating rates. It was found that the evaporation process of bio-oil can be divided into two stages. In the evaporation process of bio-oil, the heat requirements were 2.299×10^3, 2.178×10^3, and 2.072×10^3 J/g at 10, 20, and 30 °C/min, respectively. With an increase in the heating rate, the activation energy of bio-oil increased. Moreover, the response time of the heat transfer was longer than that of the mass transfer.

2. Based on GC-MS and TG-DSC analysis of bio-oil, four models with five compounds (methanol, water, ethanol, furfural, and phenol) were established to study the bio-oil evaporation process. By comparing the TG-DSC characteristics of bio-oil against the compound models, it has been found that the models can replicate mass and heat transfer in the evaporation process of bio-oil with reasonable accuracy. After a series of tests, we concluded that model 2 was the best model and the errors for activation energy of TG, activation energy of DSC, maximum endothermic rate, and total heat requirement were 3.04%, 5.88%, 2.49%, and 1.06%, respectively.

ACKNOWLEDGMENTS

The authors thank the National Basic Research Program of China (Grant No. 2013CB228103) and the Key Program of the Chinese Academy of Sciences (Grant No. KGZD-EW-304-3).

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Article submitted: March 25, 2014; Peer review completed: May 16, 2014; Revisions accepted: May 23, 2016; Published: May 29, 2014.