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Effect mechanism of dry and wet alternate ageing on wood during exothermic behaviour

Jiajia Song[1] · Jingyu Zhao[1] · Jun Deng[1] · Shiping Lu[1] · Gai Hang[1] · Yanni Zhang[1] · Chi-Min Shu[2]

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Abstract
In recent years, ancient wooden building fires have been a hot issue that has not been properly solved. The existing ancient wood buildings objectively have serious natural ageing phenomenon, among which the dry and wet alternating ageing phenomenon of wood caused by water is the most serious. However, the phenomenon of dry and wet alternating ageing pays less attention to the influence of wood combustion. Therefore, this study took the typical wood species of ancient wooden buildings as the research object, based upon the natural ageing phenomenon of these buildings, determining the artificial acceleration of dry and wet alternate ageing method, to obtain dry and wet alternate ageing wood. The thermal diffusion coefficient of dry and wet ageing wood was analysed by thermal property experiments. Using differential scanning calorimetry experiment, we appraised the change law of heat flow in the combustion process of dry and wet ageing wood, determined the characteristic peak intensity and stage continuous temperature of dry and wet ageing wood, and mastered the change characteristics of wood in different thermal release stages affected by dry and wet alternating ageing. Finally, the apparent activation energy distribution of ageing wood in different exothermic stages was calculated and analysed by isoconversion method. The influence mechanism of alternating dry and wet ageing on wood combustion thermal release behaviour was revealed. The results show that the main thermal release of dry–wet ageing is the stage of volatiles precipitation. The alternate ageing of dry and wet has the greatest impact on the energy demand of thermal response in the accelerated thermal release stage. The influence of alternating dry and wet ageing on different types of wood in the rapid exothermic stage is quite different.

Keywords Thermal diffusion coefficient · DSC · Thermal release stages · Apparent activation energy · Isoconversion method

Introduction

Ancient building fire is a more severe challenge that humans face when protecting their historical heritage [1]. Once ancient wooden buildings catch fire, they are bound to face complete destruction [2, 3]. The Bridge of Universal Peace, the longest existing wooden arcade bridge in China, has a history of more than 900 years. On 6 August 2022, a fire broke out and the bridge body burned down and collapsed, which was exceptionally painful. Therefore, it is very necessary to deeply explore the fire mechanism of ancient wooden buildings. Affected by the evolution of climate environment, ancient wooden buildings have a serious ageing phenomenon, among which the influence of moisture in the natural ageing process of water is extensive, mainly caused by climate change in the wood moisture absorption and desorption behaviour, that is, the dry and wet alternate ageing phenomenon [4–6]. This ageing is bound to cause the combustion of the ancient wooden buildings to change. Therefore, this study considers the exothermic combustion behaviour of wood from the perspective of dry and wet alternate ageing and tries to explain the influence of dry and wet alternate ageing phenomenon on the wood combustion from the change law of exothermic behaviour characteristics.

Various scholars have studied the combustion of wood [7–14] and determined the main characteristic stages of wood in the process of thermal decomposition. TranVan

✉ Jingyu Zhao
zhaojingyu2014@126.com

1 School of Safety Science and Engineering, Xi'an University of Science and Technology, Xi'an 710054, Shaanxi, China

2 Department of Safety Health, and Environmental Engineering, National Yunlin University of Science and Technology, 123, University Rd., Sec 3, Douliou 64002, Yunlin, Taiwan

et al. [15] showed that the presence of moisture can affect the thermal decomposition behaviour of wood. The kinetic analysis of the wood combustion is usually performed by Flynn–Wall–Ozawa (FWO), Kissinger–Akahira–Sunose (KAS), Kissinger, and Friedman [16, 17]. Starting from the wood itself, scholars studied the changes of the wood properties after different treatments, including heat treatment [18], vacuum freeze-drying treatment, cork and hardwood treatment [19], acid immersion treatment [20, 21], the addition of flame retardant [22] and other ways. Among them, much more attention was paid to distinguishing cork and hardwood, finding that the degradation temperature of cork extract was lower than other wood components and did not affect its thermal stability. The improvement of wood properties was mainly in the increase of carbon and the decrease of moisture; on the other hand, the heat treatment would curtail the apparent activation energy of wood chemical reaction, and the amount of gas products gradually decreased with the increase in heat treatment temperature [23, 24].

The influence of natural environmental factors on wood has always been the focus of scholars, but naturally ageing wood has too many uncertain factors, along with difficulty to obtain a large experimental amount; artificial accelerated ageing has become the main means used in the scientific research of ageing wood. Garcia, Kariz, Liu, Timar, and others used artificial accelerated ageing treatment by ultraviolet radiation, infrared radiation, natural light, and artificial xenon light, respectively, and analysed its colour stability, shear strength and anti-ageing performance under different accelerated ageing conditions [25–28]. Cheng et al. [29] and Huang et al. [30] explored the ageing phenomenon of wood and found that with the increase in ageing degree, the colour of wood gradually changed from light yellow to dark reddish brown; with the extension of ageing time, the cell wall and tube cells of wood burst, and the pores gradually cracked. Boratynski et al. [31] used the method of simulating the atmospheric environment to ageing the wood and found that accelerated ageing caused a significant reduction in the density and compressive strength of the wood. Kudela et al. [32], Liu et al. [33], Zeniya et al. [34], and others evaluated the vibration characteristics and colour changes of humid heat ageing wood. The results showed that wood was ageing at 100 °C, and the main chemical changes were lessened in hydroxyl group, increased in unconjugated group, and showed slight increase in lignin.

To sum up, much research has been carried out on the combustion of wood and on the physical and chemical changes of ageing wood. However, less attention has been paid on how the ageing affects the combustion characteristics of wood, and how the research on the dry and wet ageing affects the exothermic behaviour of wood combustion was almost blank. Therefore, this study started from the actual ageing of the ancient building wood, referring to the ageing standard, and carried out the wood dry and wet alternate ageing experiment, to acquire the dry and wet ageing wood. Based upon a thermal property experiment, the thermal diffusivity of dry and wet ageing wood was analysed. Through the DSC experiment, the heat flow change law of the combustion of dry and wet ageing wood was relatively analysed. In addition, the characteristic peak strength and the stage continuous temperature of the dry and wet ageing wood combustion exothermic behaviour were determined, mastering the change characteristics of wood combustion thermal energy release affected by dry and wet alternate ageing. Finally, the apparent activation energy distribution of ageing wood in different thermal energy release stages was calculated and analysed, and the influence mechanism of alternate dry and wet ageing on the exothermic behaviour of wood combustion was revealed. The research results aimed to provide theoretical reference for the early warning and monitoring of fire in wooden ancient buildings.

Experimental

Samples

According to the survey of Chinese ancient architecture wood structure timber species and the measured analysis of the main timber properties, the typical ancient wood types, pine, elm, and fir were selected as the main research objects.

Artificially accelerated experiment of alternating dry and wet ageing

The alternate ageing of dry and wet in the natural environment was mainly the physical ageing of the polymer molecules constantly asymptotically returning to equilibrium during the alternate action of adsorption and desorption. Therefore, this study referred to the ISO 56601, JSTM J 7001 and NT FIRE 053.A. [35–37]. Artificial acceleration simulation experiments were conducted from the moisture absorption and desorption of wood in atmospheric environment.

Because ancient wood buildings have existed for a long time, the natural dry and wet alternate ageing behaviour is more severe; the way of simulated wood water absorption and desorption was set in the extreme environmental conditions. The drying temperature of 100 °C was selected to simulate the desorption process of atmospheric wood moisture, and the wood was completely soaked to simulate the absorption of atmospheric moisture. In the experimental test, it was found that the mass of wood changed prominently in the first 10 h during the 0−16-h immersion. The mass of wet swollen wood changed significantly in the first 6 h of 0−14 h of drying. Therefore, the sample was first soaked

Table 1 Proximate analysis of dry and wet ageing wood

Type of wood	Fresh and ageing wood	M_{ad}/ %	A_{ad}/ %	V_{ad}/ %	FC_{ad}/ %
Pine	Fresh wood	9.09	0.17	79.60	11.14
	Ageing wood	4.26	0.32	80.08	15.34
Elm	Fresh wood	8.51	0.88	73.99	16.62
	Ageing wood	3.82	0.86	78.51	16.81
Fir	Fresh wood	8.41	0.36	78.72	12.51
	Ageing wood	6.10	0.30	76.76	16.14

in water for 10 h and then removed and placed in a dry box environment for 6 h, which was defined as an alternate dry and wet ageing cycle. A total of 60 cycles were performed per sample. The size of the experimental wood was referred to a previous study [38] and was set to $100 \times 100 \times 10$ mm^3.

Table 1 shows the results of proximate analysis experiment before and after dry and wet ageing of each wood. Because of the influence of alternate dry and wet ageing, the moisture of ageing wood was reduced more than that of fresh wood.

Thermoactivity experiment

The LFA 457 laser flash device (Germany) was used, and the reference model was the thermal diffusion coefficient model equation proposed [39–41]. Wood is a heterogeneous material, and the thermal properties of different orientation samples are different. Therefore, in the experiment, the wood was first broken, and the screening particle size was 80−120 mesh, and the pressing device was used for pressing. The specific experimental conditions are summarised in Table 2. A temperature collection point was set every 15 °C, atmosphere was air, flow was constant at 100 mL min^{-1}, and heating rate was set at 1 °C min^{-1}.

Thermal analysis experiment

The experimental instrument used in this study was the STA449F3 thermal analyser. The sample was ground to 80−120 mesh, the experimental gas flow rate was controlled at 100 mL min^{-1}, the temperature range was 40−600 °C, and the sample mass was 5.0 ± 0.2 mg. The specific experimental conditions are displayed in Table 3.

Results and discussion

Effect of dry and wet alternate ageing on thermal diffusion of wood

Thermal diffusivity characterises the diffusion ability of the heat flow. According to Fig. 1, the change trend of the three experimental woods was the same, all showing a linear decline mode with temperature growth. Compared with the three experimental woods, the changes of wood before and after ageing were different. The thermal diffusion ability of pine and fir increased after ageing, while elm decreased. This was due to pine and fir belonging to cork, and the mechanical creep of pine and fir was stronger after absorption and desorption of the same intensity of water than that of elm [42–44]. With the alternate ageing of dry and wet, the internal pores of the wood gradually became loose, the internal tissue gradually fell off, and the pore spacing gradually increased. Furthermore, elm belongs to hardwood, less affected by mechanical creep, although the water absorption and reconciliation to attract the internal tissue to became loose, but the internal pore changes were small, resulting in the disorder of elm tissue; its thermal diffusion ability decreased more than the fresh wood. Notably, the fit slope of the thermal diffusivity increased in all three woods after

Table 2 Experimental conditions for thermoproperty test

Type of wood	Fresh and ageing wood	Diameter/ mm	Thickness/ mm	Mass/ g	Density/ g cm^{-3}
Pine	Fresh wood	13.01	1.14	0.1566	1.033
	Ageing wood	12.77	0.98	0.1491	1.188
Elm	Fresh wood	12.89	1.00	0.1409	1.08
	Ageing wood	12.82	0.95	0.1508	1.23
Fir	Fresh wood	13.03	1.11	0.1457	0.984
	Ageing wood	12.70	0.98	0.1499	1.207

Table 3 Experimental conditions of thermal analysis

Type of wood	Fresh and ageing wood	Atmosphere	Heating rate/ °C min^{-1}
Pine	Fresh wood, ageing wood	Air	10, 20, 30, 40
Elm	Fresh wood, ageing wood	Air	10, 20, 30, 40
Fir	Fresh wood, ageing wood	Air	10, 20, 30, 40

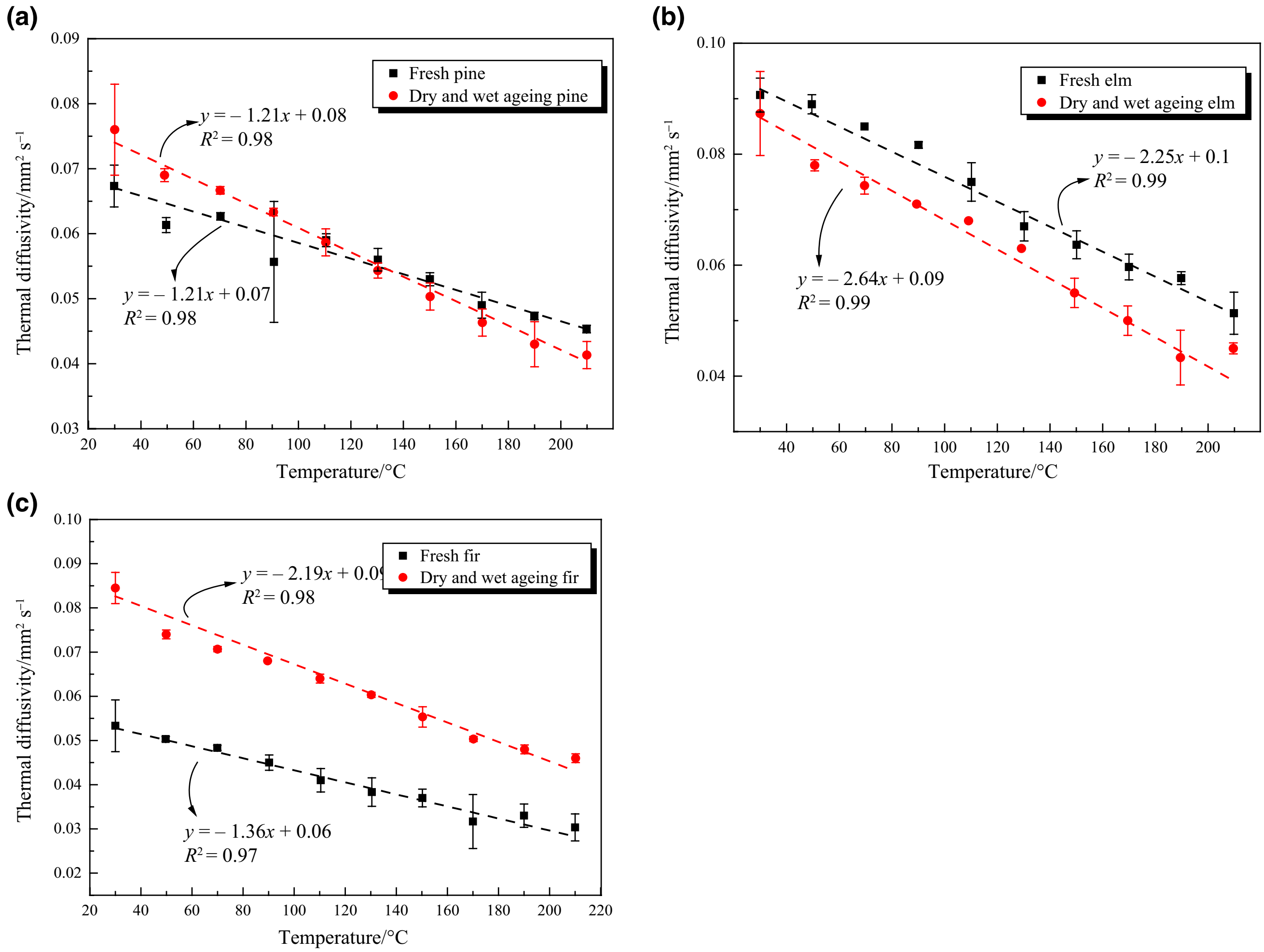

Fig. 1 Thermal diffusivity of fresh wood and ageing wood varies with temperature: **a** pine, **b** elm, and **c** fir

ageing. That is, the sensitivity of the thermal diffusion ability to the influence of temperature increased after ageing.

Analysis of dry and wet ageing on the evolution of wood heat flow

Heat flow

As shown in Figs. 2–4, the heat flow curves showed consistent reaction processes, and they all demonstrated the same evolutionary characteristics. As the temperature increased, the growth trend of the heat flow gradually changed, and the first inflection point temperature was 310−370 °C, then entering another exothermic reaction stages. After the second peak, the curve dropped almost vertically. Comparing the heat flow before and after dry and wet ageing of the three experimental woods, it was found that the temperature range of the overall reaction process of dry and wet ageing wood was reduced more than that before dry and wet ageing. According to the analysis, this was the joint effect of the alternate ageing promoting the large decreased of wood moisture content, the altered thermal transfer of wood cell wall pore, and the hemicellulose glass transition. Because elm is a hardwood and has less lignin content, its reduction was the most extensive. Note that in the dry and wet ageing elm, the two exothermic peaks overlapped at the heating rate of 40 °C min^{-1}. On the other hand, the heating rate was accelerated, and the dry and wet ageing decreased the temperature range required for combustion.

Effect of the heating rate

The most prominent effect of the heating rate on the thermal release of wood combustion was that increasing the heating rate shifted the peak heat flow to the high-temperature region. The effect of the heating rate on the heat flow (Fig. 5) of ageing wood is discussed below. Under different heating rates, was the main contradiction conversion

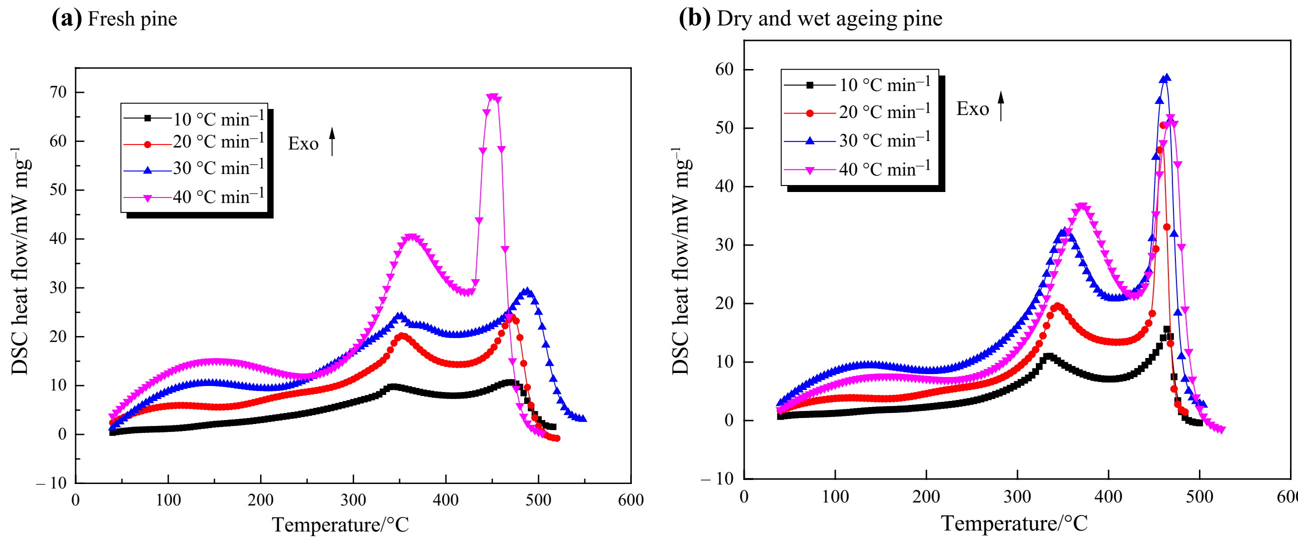

Fig. 2 Curves of pine heat flow changing with temperature before and after dry and wet ageing

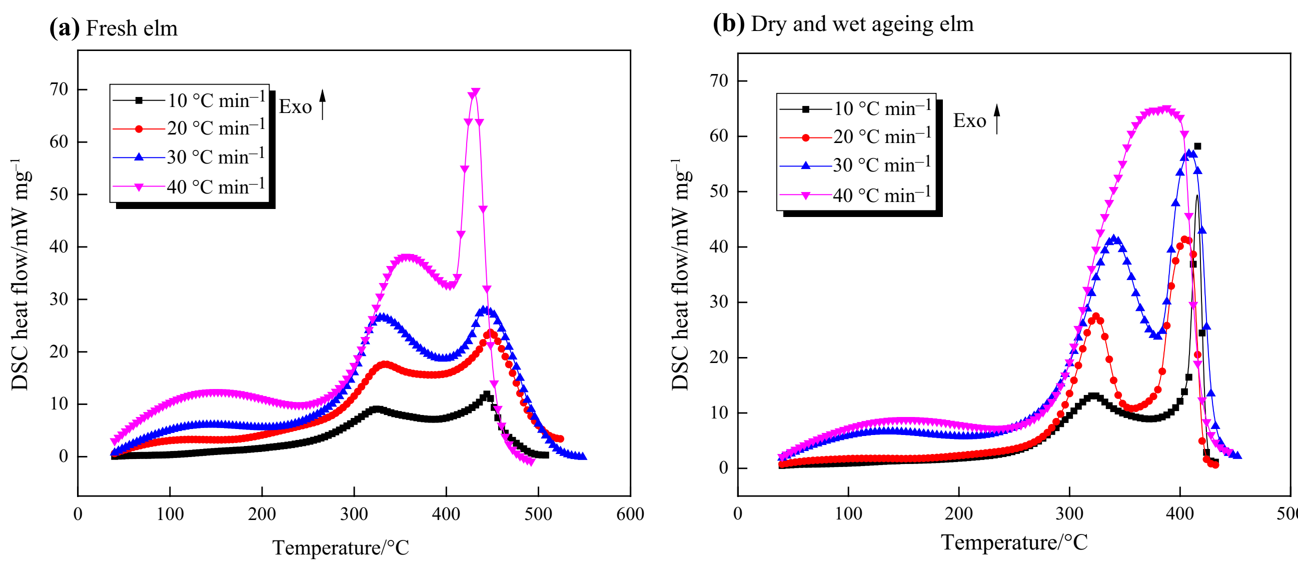

Fig. 3 Curves of elm heat flow changing with temperature before and after dry and wet ageing

of the same reaction stage. On the one hand, the reaction involved in the wood tissue structure released thermal energy; on the other hand, the tissue pore affected its energy transport and release. When the heating rate was low, the reaction phase lasted longer, and the wood tissue structure participated in the thermal reaction degree, making it wider. On the heat flow curve, the peak and valley appeared in the initial phase of 10 °C min^{-1}. When the heating rate was fast, although the thermal reaction of wood went through a stage transition, the degree of transition was low. When the temperature was too high, the reaction was still continuing, and the reaction was synchronised with the next stage. In the heat flow curve, at the heating rate of 30 °C min^{-1}, the growth rate of the heat flow decreased or gently occurred in the middle of the reaction. When the heating rate was too fast, the time of the wood reaction was too short, and the exothermic reaction at the stage that should have appeared did not occur, resulting in an energy vacancy. On the heat flow curve, at 40 °C min^{-1}, the curve declines at around 150 °C, and the heat flow growth rate was negative (Fig. 5b).

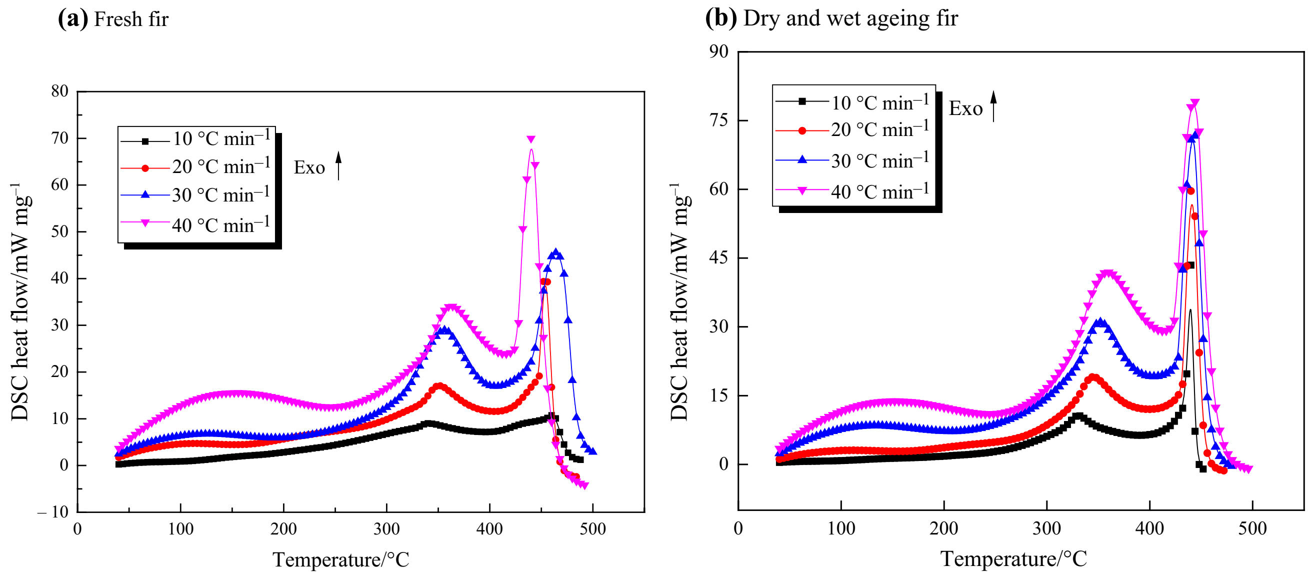

Fig. 4 Curves of fir heat flow changing with temperature before and after dry and wet ageing

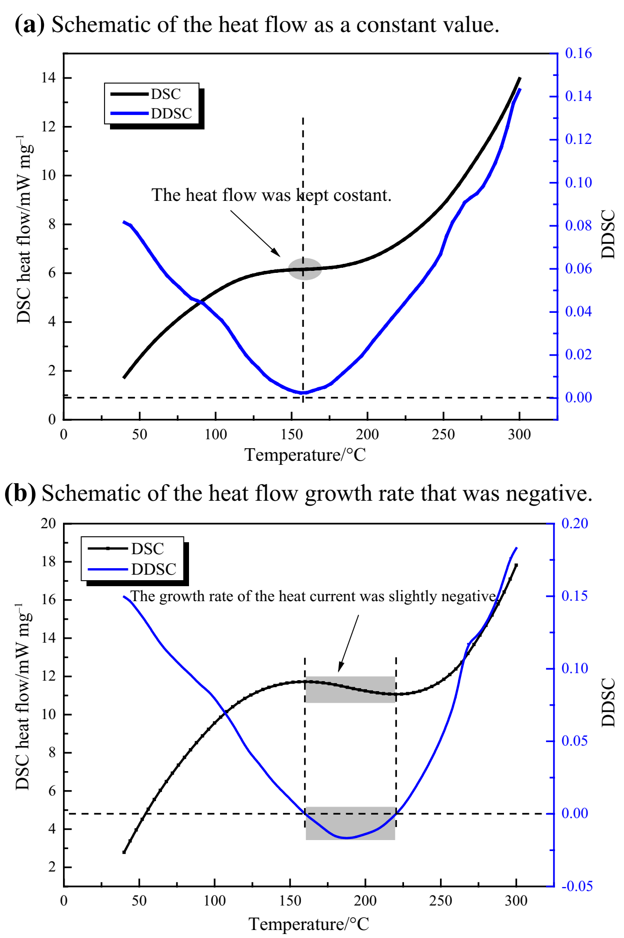

Fig. 5 Characteristic temperature range of the heat flow at different heating rates

Division of the reaction stages based upon the heat flow

Since the thermal reaction at different stages of the wood was presented well at 10 °C min^{-1}, the stage division here was taken at 10 °C min^{-1}. The heat flow curve was derived to obtain the DDSC curve. To phase and divide the thermal release more accurately, the curve was guided quadratically to obtain the DDDSC curve, as shown in Fig. 6. We divided the thermal release process into four stages according to the trend of heat flow. The first stage was the dehydration stage. In the early stage of the experiment, wood contained a certain amount of water; the thermal release of wood and the heat absorption of water evaporation were carried out at the same time. The thermal release was less than the thermal needed for water evaporation; the macroscopic performance was the thermal absorption state. The second stage heat flow value changed less, and cellulose was pyrolysis in wood, which was the volatiles precipitation stage. In the third stage, the first exothermal peak appeared, which was the volatile combustion phase, governed by the thermal decomposition of hemicellulose, cellulose, and partial lignin. The fourth stage was the second peak stage, mainly carbon oxidation reaction.

Effect of dry and wet ageing on characteristic peak of heat flow

The peak of the wood heat flow curve at different heating rates were counted, as illustrated in Figs. 7 and 8. As can be seen from Fig. 7, the peak combustion temperature of volatiles of ageing wood was 5−15 °C earlier than that of fresh wood, and the peak temperature advance phenomenon occurred. That is,

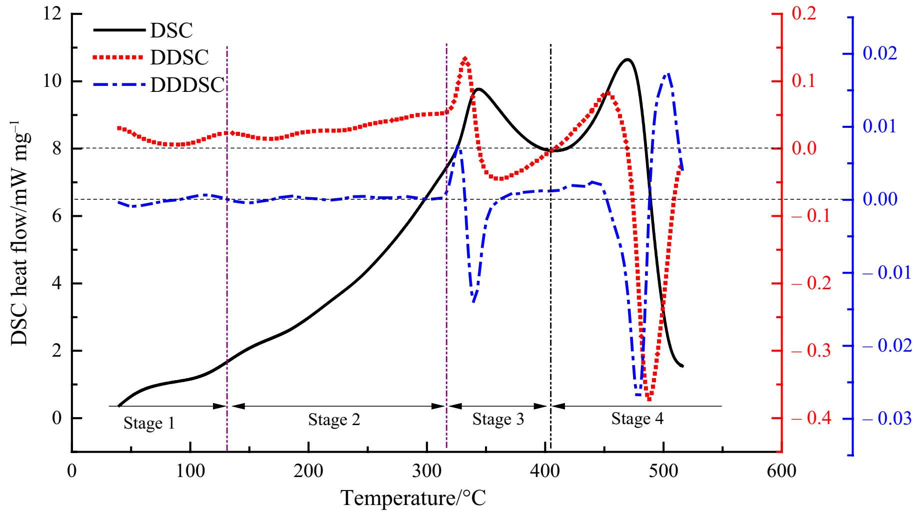

Fig. 6 The heat flow was divided along with the temperature change stage

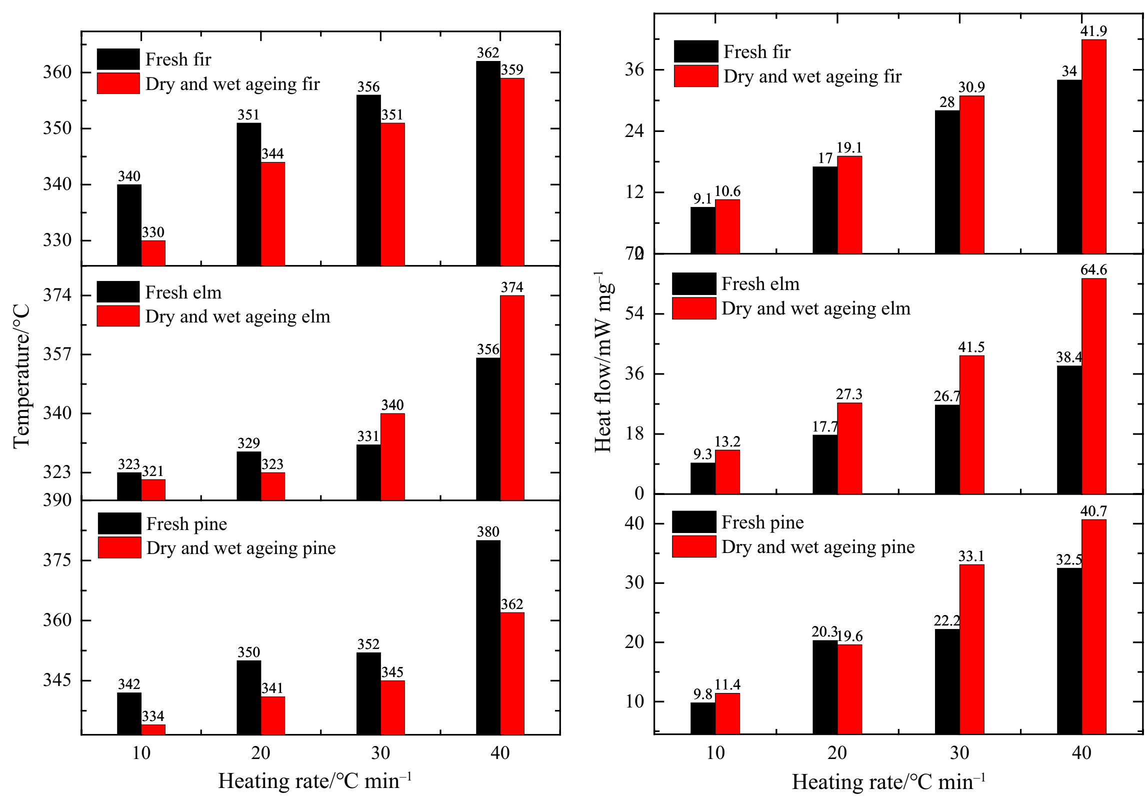

Fig. 7 Peak and peak temperature of the heat flow in the volatile combustion stage of the three experimental woods varied with the heating rate

at a lower temperature, the wood volatile combustion can reach the maximum exothermic strength. The main reason for the volatile combustion peak moving forward is that the surface of the cell wall broke due to the influence of stress in the suction and desorption cycle, the free volume inside the wood increased, the obstruction of gas precipitation decreased, and the volatile precipitation was fast, the peak moved forward. Note that the peak temperature of the dry and wet ageing elm was greater than the fresh elm at 30 and 40 °C min^{-1}. In addition, the peak of dry and wet ageing wood was basically larger than that of fresh wood, and the peak of elm had the biggest difference. On the one hand, because of the high density of elm and the high porosity of pine and fir, when the pore was affected by the same creep effect, the process obstruction of volatile precipitation was curtailed, and the second was that

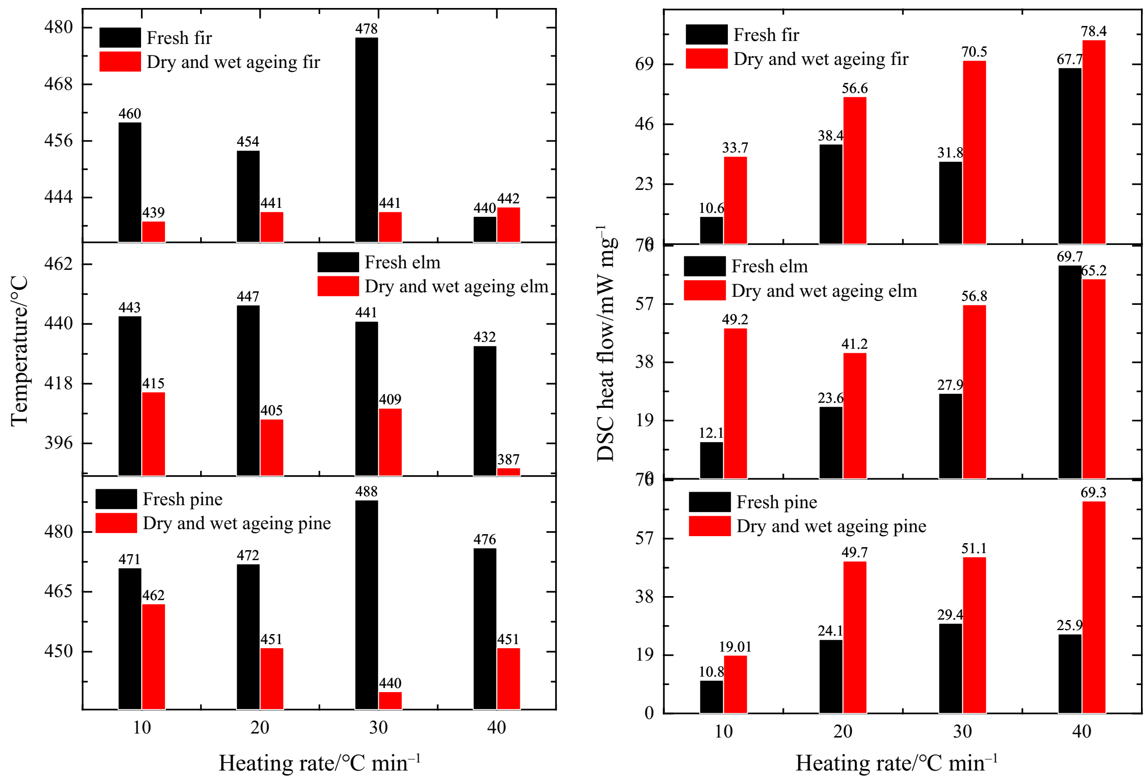

Fig. 8 Peak and peak temperatures of carbon combustion varied with the heating rate

the texture of elm is hard, and the consumption of volatile substances in the dry and wet ageing process was less.

As demonstrated in Fig. 8, the peak temperature did not increase with the heating rate of carbon combustion. It was due to the carbon and oxygen reaction stage of the wood structure having an intense exothermal reaction. The thermal energy production was more governed by the internal control of the wood, and the change of external conditions had less impact on it [45]. In general, the strength of wood carbon combustion peak changes greatly before and after dry and wet ageing. The peak temperature of dry and wet ageing wood was less than that of fresh wood, and the overall temperature was shifted forward by 20–45 °C. It was mainly because the alternate ageing of dry and wet led to the degradation of wood hemicellulose and cellulose. Second, the change of the thermal transfer mechanism in the pore caused the forward movement of the volatile combustion peak, which reduced the combustion contribution rate of wood volatilisation in the process of carbon combustion.

Dry and wet ageing effect on wood thermal energy release

Thermal energy release analysis

The abscissa of the heat flow curve was converted into time and integrated to obtain the change curve of wood thermal energy release with temperature, as depicted in Fig. 9. Under the same heating rate, the exothermal of ageing wood and fresh wood had similarly changed. In the initial stage of the experiment, the thermal energy release was weak, and with the increase of the temperature, the thermal energy release gradually increased and then increased exponentially. The change of thermal energy release of the three types of wood did not increase with the heating rate, indicating the growth of winding and occlusion.

The thermal energy release curves of the experimental wood before and after dry and wet ageing under different heating rates were compared. At 10 °C min^{-1}, ageing

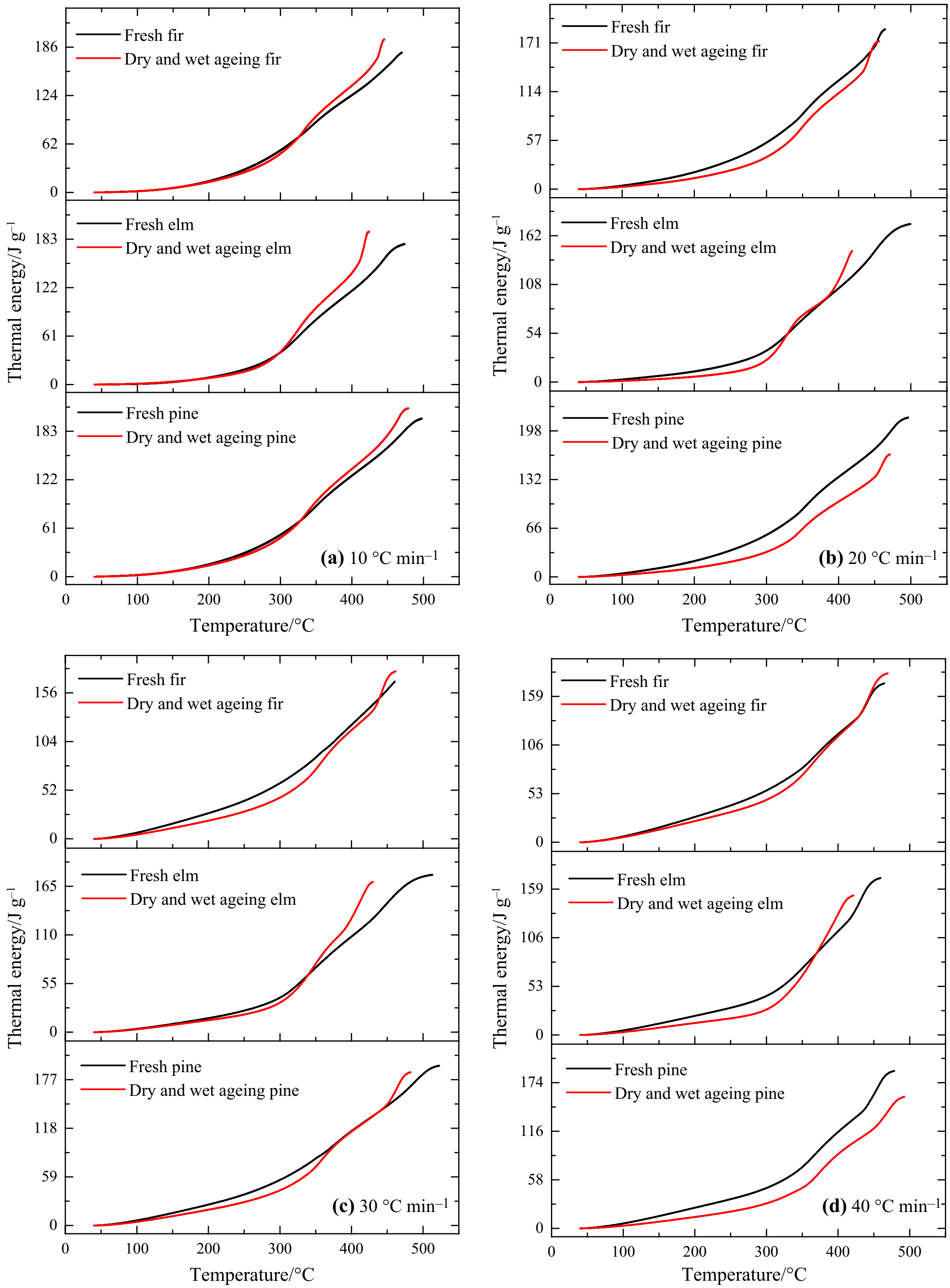

Fig. 9 Thermal energy release change curve with temperature tested by DSC

and fresh wood of pine, elm, and fir had intersections at 330, 296, and 325 °C, respectively. In the beginning of the experiment, the thermal energy of fresh wood was greater than that of ageing wood. With the increase in temperature, the thermal energy release difference before and after ageing increased first and then shrank, when the temperature was greater than the intersection point, the dry and wet ageing wood thermal energy release gradually increased more than the fresh wood, and the gap gradually increased until the end of the experiment.

At 20 °C min^{-1}, the comparison of the woods thermal energy was different before and after dry and wet ageing. During the entire combustion, the thermal energy of dry and wet ageing pine and fir was lower than that of the fresh wood, while the thermal energy of elm wood was greater than that of the fresh wood after the temperature was more than 330 °C. In the low temperature stage, the fresh wood had also entered a rapid growth period ahead of schedule than the dry and wet ageing wood. Under different heating rates, the intersection of the fir thermal energy release curve before and after dry and wet ageing was in the carbon combustion stage at the end of the experiment. In addition, the thermal energy release of elm before and after dry and wet ageing existed at an intersection point, which was in the mid-experimental volatile combustion stage, and the intersection temperature increased continuously as the heating rate increased. Note that in the early stage of the experiment, that is, before the wood caught fire, the thermal energy of the fresh wood was greater than the dry and wet ageing wood. The results showed that the temperature of the dry and wet ageing wood was closer to the ignition temperature, which needs special attention in the actual fire thermal sensing detection of ancient buildings.

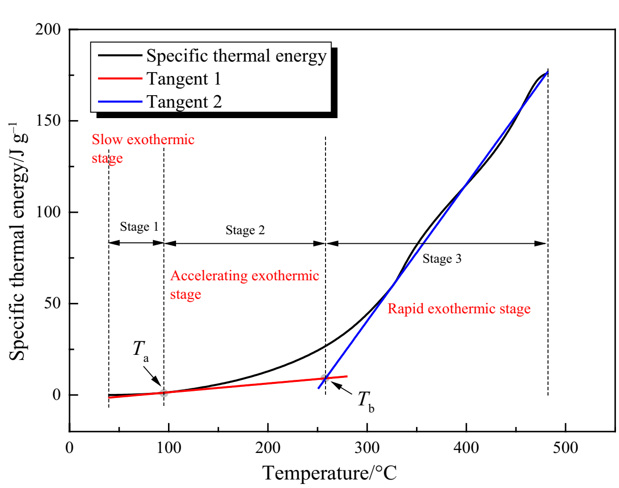

Fig. 10 Schematic of the stage division of the thermal energy release

Thermal energy release stage division

The thermal energy release of wood presents obvious periodic characteristics. Shown in Fig. 10 are the beginning and end of the thermal energy release curves. The first stage was when the heat flow changed from the initial exothermic temperature to the cutting point temperature T_a, the change of the heat flow was relatively slow, and defined as the slow exothermic stage. The second stage was the temperature range from T_a to the intersection of the two tangents. The upward trend of the thermal energy release was substantially accelerated, and it was defined as the accelerated exothermic stage. T_b until the end of the experiment was the third stage, defined as a rapid exothermic stage. Here, T_a was selected as the end point of the first phase of the heat flow curve. According to the exothermic, compared with the previous study [12, 46], T_a was defined as the dehydration end temperature and T_b as the ignition temperature.

Table 4 shows the corresponding boundary temperatures of the three experimental woods. The end of dehydration temperature of fresh wood was greater than that of dry and wet ageing wood, while the ignition temperature of dry and wet ageing wood was greater than that of fresh wood. As shown in Fig. 11, fitting the ignition temperature changed with the heating rate; it was found that both pine and elm showed a linear growth with the heating rate. Since pine thermal diffusivity intersected with temperature change, pine ignition temperature increased with heating rate after dry and wet ageing, and the gap with fresh wood gradually shrank, while elm increased and the difference with fresh wood gradually increased. The fir grew exponentially with the heating rate.

Table 4 Boundary temperature of the wood at different heating rates

Type of wood	Heating rate/ °C min^{-1}	Fresh wood		Ageing wood	
		T_a/ °C	T_b/ °C	T_a/ °C	T_b/ °C
Pine	10	131	249	121	276
	20	135	274	152	293
	30	138	280	137	302
	40	168	297	166	315
Elm	10	132	266	119	277
	20	140	281	128	293
	30	146	284	136	302
	40	157	295	149	317
Fir	10	134	252	121	269
	20	139	277	132	291
	30	143	283	138	301
	40	162	287	158	304

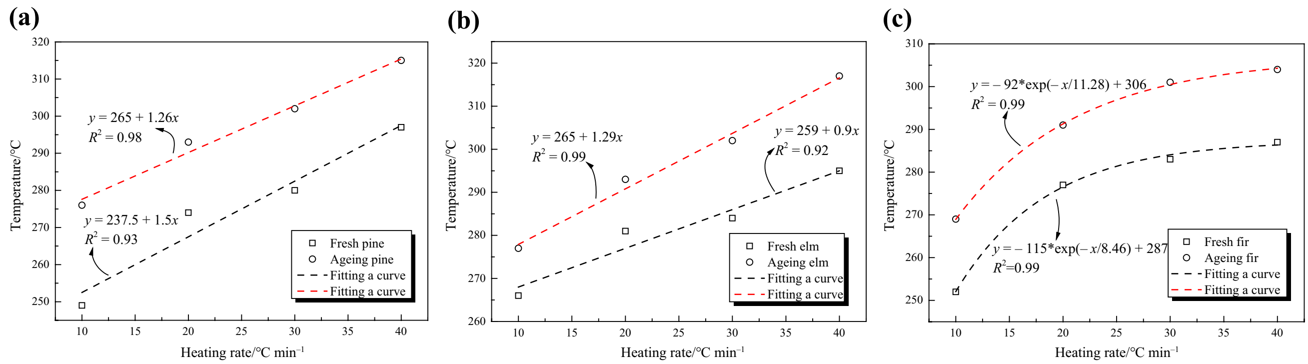

Fig. 11 Experimental wood ignition temperature was fits with the heating rate

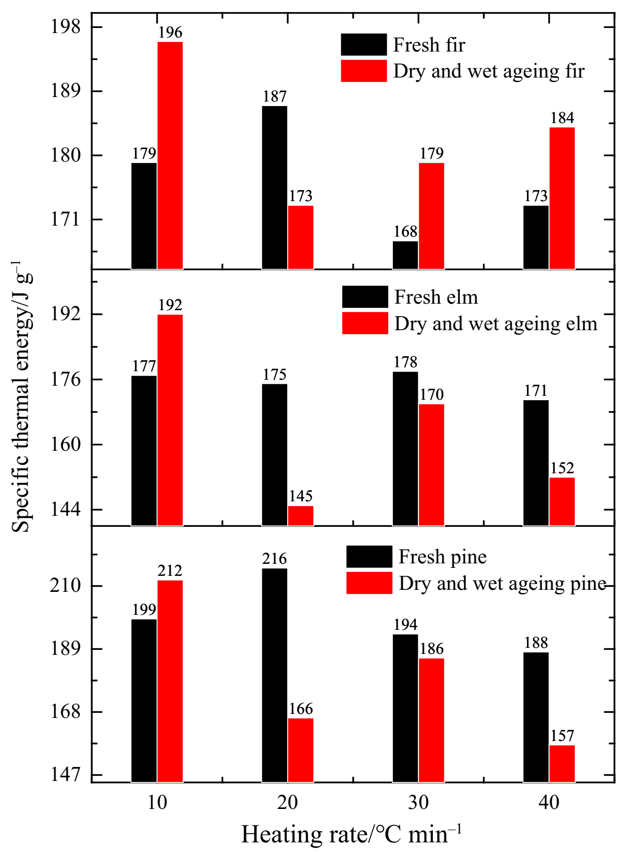

Fig. 12 Comparison of total thermal energy release before and after dry and wet ageing under different heating rates

Total thermal energy release

The total thermal energy release of dry and wet ageing wood and fresh wood is shown in Fig. 12. The total thermal energy release of wood did not monotonically increase or decrease with the increased heating rate, which was related to the runaway thermal energy release of wood during the carbon combustion stage. Because the total heat release was calculated from after the system completely entered the state of thermal energy release, the difference of the total thermal energy release size should be caused by the change of the internal microstructure and the different heat reactions in the wood. As can be seen from Fig. 12, at 10 °C min^{-1}, the total thermal energy release of wood after dry and wet ageing was greater than that of fresh wood, and the difference range was between 13 and 17 J g^{-1}. In terms of the total release heat release gap, the wood difference was largest before and after dry and wet ageing at 20 °C min^{-1}, while the difference was smallest at 30 °C min^{-1}. It was inferred that there was a critical heating rate between 20 and 30 °C min^{-1}, and the total thermal energy release would jump in the heat reaction of dry and wet ageing wood; the effect of dry and wet ageing on this mutation temperature rate point needed to be further discussed. It is worth noting that the higher total thermal energy release of wood fluctuated remarkably with the higher growth of heating rate than the fresh wood, revealing that the dry and wet ageing wood was more sensitive to heating rate and also indirectly indicated that the external environment would provide more interference to the combustion of wood after dry and wet ageing.

Apparent activation energy

To analyse the apparent activation energy distribution pattern of the wood thermal reaction more accurately, we calculated the apparent activation energy of dry and wet ageing wood at 10, 20, and 40 °C min^{-1}. To grasp the influence of the dry and wet heat ageing of wood, the wood in the accelerated exothermic stage and rapid exothermic stage was defined as a complete reaction, namely the reaction process from the dehydration temperature to the ignition temperature as 1, the ignition temperature to the end of the combustion stage of the reaction process as 1. The distribution of apparent activation energy of dry and wet ageing wood in different exothermic stages with the reaction process was computed according to the Friedman differential isoconversion method

[47]. The logarithmic form of the Arrhenius equation is expressed in Eq. (1):

$$\ln\left(\frac{d\alpha}{dt}\right)\alpha, i = \ln\left[A\alpha f(\alpha)\right] - \frac{E\alpha}{R \cdot T_{\alpha,i}} \quad (1)$$

where i is the different temperature processes; $T_{\alpha,i}$ is the temperature at which the conversion degree α is obtained under the conditions of its temperature change.

$$\beta = \frac{dT}{dt} = \text{const} \quad (2)$$

β is the heating rate. Equation (2) can be transformed into Eq. (3):

$$\ln\left[\beta\left(\frac{d\alpha}{dT}\right)\alpha, i\right] = \ln\left[A\alpha f(\alpha)\right] - \frac{E\alpha}{R \cdot T_{\alpha,i}} \quad (3)$$

For each given α, linear fitting of $\ln[\beta(d\alpha/dT)_{\alpha,i}]$ as a function of $1/T_{\alpha,i}$ was carried out. The apparent activation energy can, in turn, be obtained from the slope of the fitted curve. Figures 13 and 14 delineate the linear regression plots under different conversion degrees in the accelerated exothermic stage and the rapid exothermic stage, respectively.

Accelerated exothermic stage

The accelerated exothermic stage is mainly the volatile combustion stage before the wood catches fire. As shown in Fig. 15, in the stage of accelerated exothermic, the apparent activation energy distribution law of fir before and after dry and wet ageing was basically the same. With the increase of the conversion degree, the apparent activation energy first increased and then decreased, and the inflection point appeared at $a = 0.3$. The apparent activation energy of pine before and after dry and wet ageing changed in the opposite trend. The apparent activation energy of dry and wet ageing pine gradually increased with the advancement of the reaction, while that of fresh pine gradually decreased. The apparent activation energy of elm decreased rapidly between $\alpha = 0.2-0.5$; after the conversion degree exceeded 0.6; the opposite trend changed before and after dry and wet ageing. According to the previous analysis, it was mainly due to the change of heat transfer characteristics of wood pores. The change of the pore heat transfer causes changes in volatile diffusion. In the early stage of the reaction, the pores of the fresh wood were arranged neatly. With the increase of temperature, the pores gradually deformed, the gas flow rate increased, the difficulty of volatile precipitation was curtailed, and the reaction energy demand was alleviated. However, the ageing pine has enhanced pore thermal transport capacity due to the plastic deformation of creep stress, and the volatile precipitation is less difficult, and as the volatiles are gradually depleted, the reaction demand for energy gradually increases.

Comparing the apparent activation energy of the three types of wood in the early and late stage of the reaction, it can be found that in the initial reaction, the apparent activation energy of wood after dry and wet ageing was less than that before ageing, and the dry and wet alternate ageing reduced the energy barrier of wood exothermic behaviour, making the fire more likely occur. At the end of the accelerated exothermic stage, dry and wet ageing pine and fir apparent activation energy was greater than the fresh wood. The analysis believes that in the process of continuous dry and wet alternation, although the change of pore heat transfer characteristics prompted the required energy reduction in volatile precipitation, the extracts inside the wood gradually coagulated under the influence of thermal effect, causing an increase in the energy required to participate in chemical reactions during the combustion. It indicates that dry and wet ageing would increase the difficulty of wood reaction process in the volatile combustion stage.

The average apparent activation energy of the wood during the accelerated exothermic stage was determined before and after dry and wet ageing. The average apparent activation energy of pine, elm, and fir before ageing was 107.56, 202.92, and 114.33 kJ mol^{-1}, respectively, and that after dry and wet ageing was 74.94, 86.24, and 105.21 kJ mol^{-1}. After dry and wet ageing, the wood was less than fresh wood, which further indicated that dry and wet ageing would reduce the reaction difficulty of wood reaction in the accelerated exothermic stage. On the other hand, by comparing the three types of wood, it was found that the average apparent activation energy of the elm before ageing was the largest, while the fir after ageing was the largest. Second, dry and wet ageing caused the order before and after the exothermic reaction of different wood species. Before the dry and wet ageing, the elm response energy demand was the largest, and after the dry and wet ageing, the fir was the most difficult to generate thermal release. According to the difference between the average apparent activation energy before and after wood ageing, it was known that dry and wet ageing had the greatest impact on elm in the accelerated exothermic stage.

Rapid exothermic stage

The rapid exothermic stage is mainly the combustion process of carbon, and the apparent activation energy of the experimental wood in the rapid exothermic stage changes with the reaction process, as shown in Fig. 16. The apparent activation energy change trend of the three types of wood was basically the same, all increased with the conversion degree. The apparent activation energy of pine and fir increased first slowly and then rapidly with the reaction process, indicating

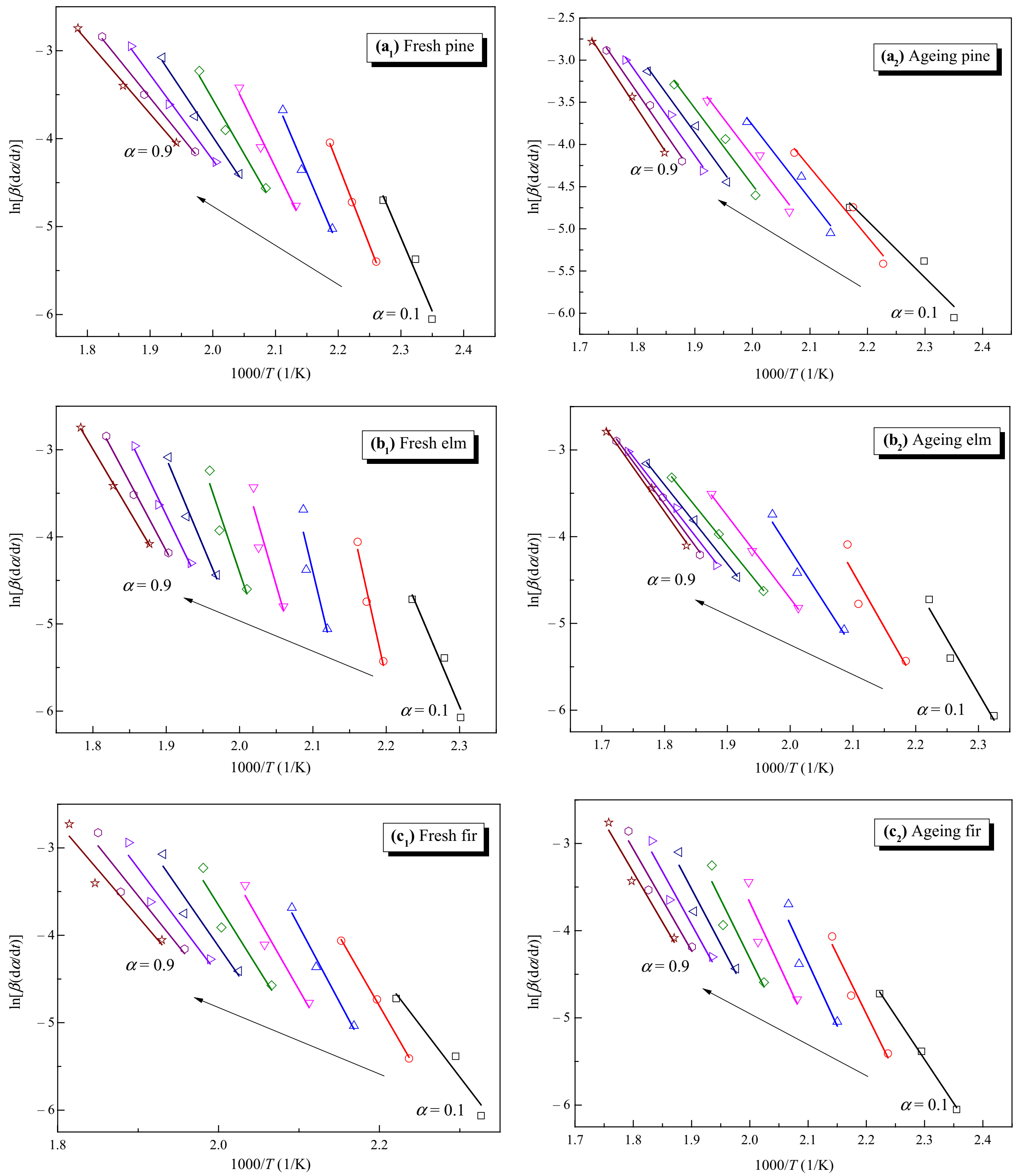

Fig. 13 The accelerated exothermic phase, $\ln[\beta(d\alpha/dT)_{\alpha,i}]$ changes in linear regression with $1/T_{\alpha,i}$: **a** pine, **b** elm, and **c** fir

that the alternate dry and wet ageing did not change the kinetic mechanism of wood in the rapid exothermic stage. In the initial stage of the rapid exothermic stage, the apparent activation energy of dry and wet ageing elm was basically in a horizontal and straight line form, while the fresh elm fluctuated up and down. The conversion degree of the fresh elm increased swiftly after more than 0.5, while the dry and wet ageing elm was greater than 0.4, earlier than the fresh

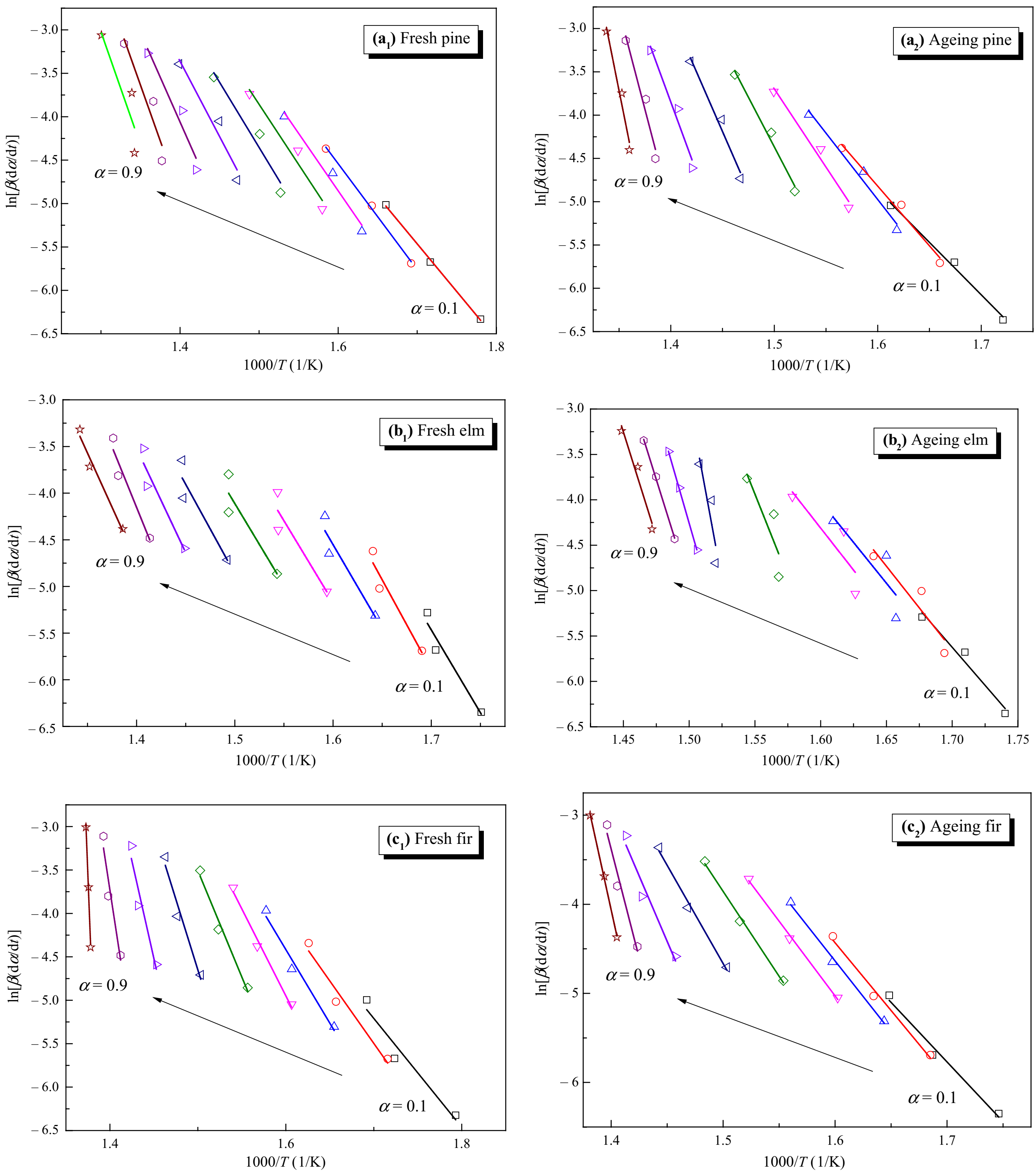

Fig. 14 The rapid exothermic phase, $\ln[\beta(\mathrm{d}\alpha/\mathrm{d}T)_{\alpha,i}]$ changes in linear regression with $1/T_{\alpha,i}$: **a** pine, **b** elm, and **c** fir

elm. The peak of the fresh elm was at 0.9, while the dry and wet ageing elm was at 0.7, also earlier than the fresh elm. This was because the total amount of volatiles contained in the fresh wood was certain, and the dry and wet alternate ageing resulted in the volatiles spreading to the wood surface in advance, and the chemical reaction occurred in advance, leading to the overall reaction process to move forward.

By comparing the apparent activation energy distribution of the three types of wood at the early reaction stage and the late rapid exothermic stage, it was found that the apparent

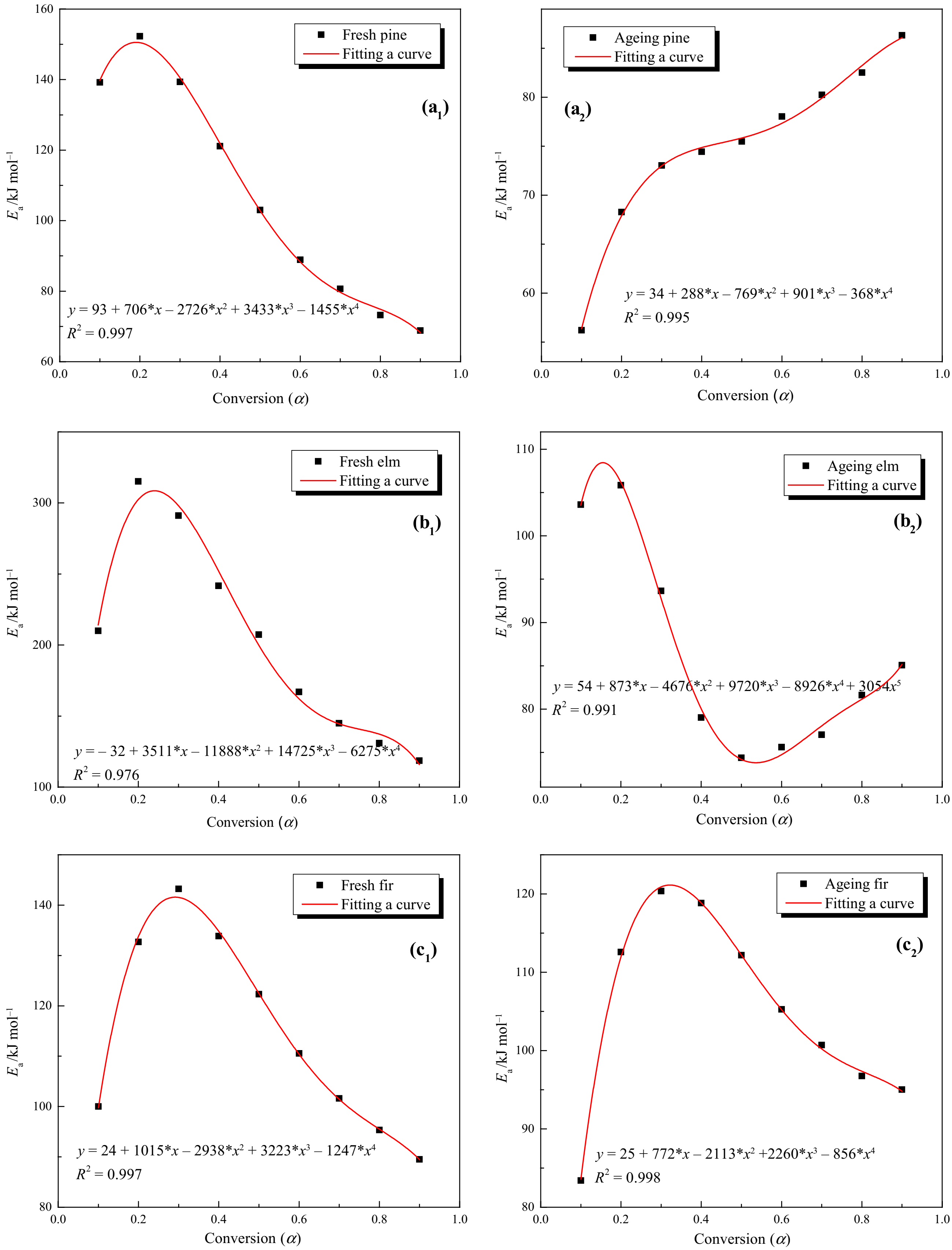

Fig. 15 Distribution trend of apparent activation energy with conversion of three experimental woods in the accelerated exothermic phase: **a** pine, **b** elm, and **c** fir

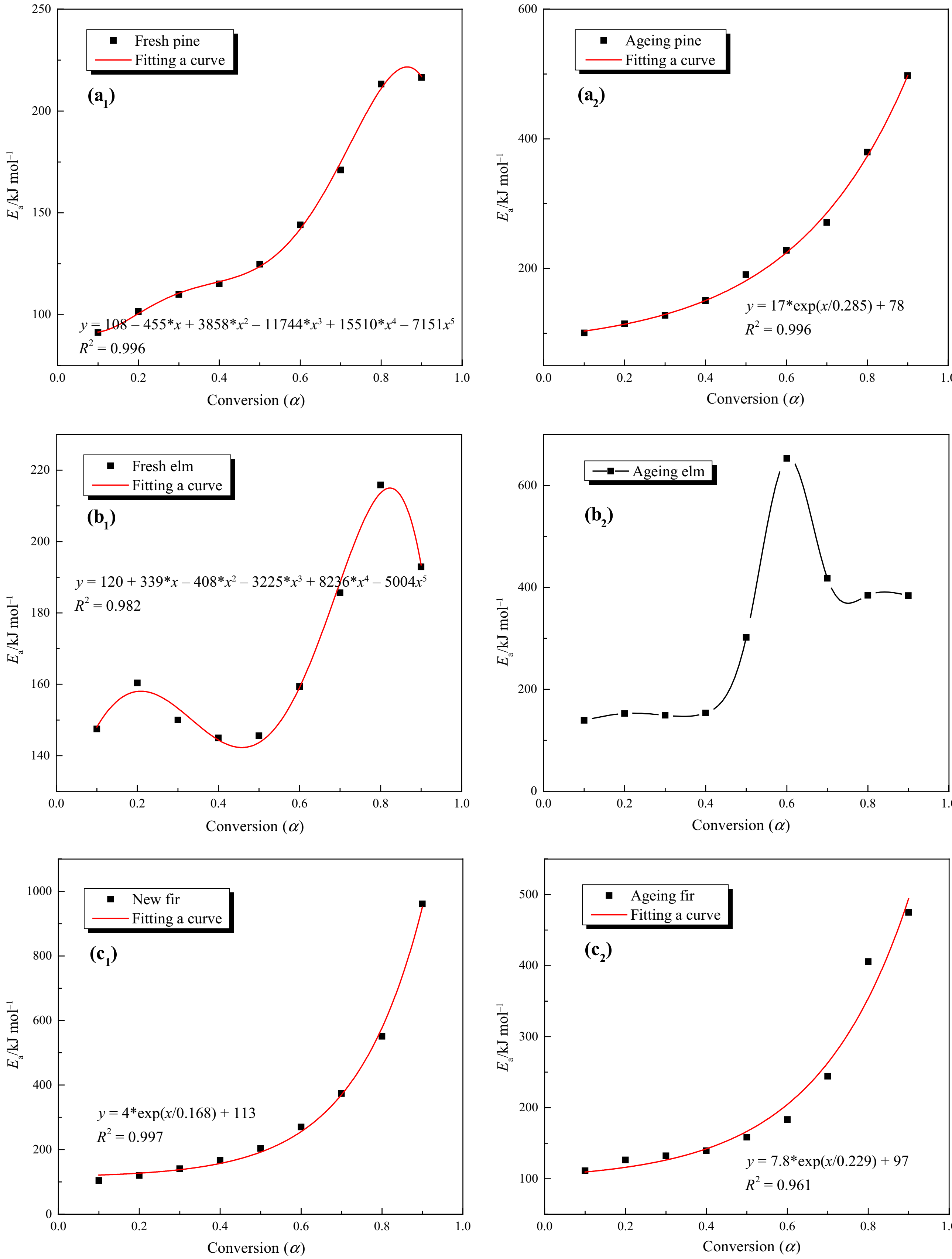

Fig. 16 Distribution trend of apparent activation energy with conversion degree of three experimental woods in the rapid exothermic phase: **a** pine, **b** elm, and **c** fir

reaction energy difference of wood in the beginning of dry and wet ageing was negligible, while the difference at the reaction end of the stage was large. The apparent activation energy of ageing pine and elm was nearly threefold that of fresh wood. It was mainly due to the dry and wet process of wood cell wall dry shrinkage fold, hardness increase, and mechanical relaxation causing some loose surface groups; the active group of carbon and oxygen chemical reaction decreased. With the advancement of the reaction process, the energy demand of ageing wood increased, and the growth of apparent activation energy was accelerated. The apparent activation energy of ageing fir here was reduced compared with that of fresh fir, which was greatly related to the change of pore thermal transfer characteristics. From the comprehensive analysis of thermal property, we know that the alternate ageing of dry and wet had the greatest interference to the pore heat transfer of fir.

The average apparent activation energy of wood in the rapid exothermic stage before and after dry and wet ageing was calculated. The average apparent activation energy of pine, elm, and fir was 143.05, 166.9, and 321.16 kJ mol^{-1}, respectively, and the average apparent activation energy after dry and wet ageing was 228.8, 304.08, and 219.56 kJ mol^{-1}. The average apparent activation energy of both the pine and elm after dry and wet ageing increased, while the elm increased more, which was related to the continuous loss of active tissue during the ageing. The performance of fir was different from elm and pine, and the apparent activation energy became smaller after dry and wet ageing, which also indicated that by the transformation of pore heat transfer, the impact of dry and wet ageing on the carbon combustion reaction energy demand of different types of wood was not uniformly increased or decreased, and different woods had great differences. Consistent with the accelerated exothermic stage, the alternating dry and wet ageing process changed the order of the difficult reaction of different wood in the carbon combustion phase. The energy barrier of fir before dry and wet ageing was the largest, while the elm was the largest after dry and wet ageing. It can be observed from the change of the apparent activation energy of ageing wood and fresh wood that the alternating dry and wet ageing had the greatest impact on elm combustion.

Conclusions

Four main conclusions were drawn from this study:

- Affected by the alternate ageing of dry and wet, the moisture of the ageing wood was lower compared with the fresh wood. Dry and wet ageing enhanced the thermal diffusion ability of cork combustion process and weakened the hardwood. The sensitivity of the thermal diffusion ability to the influence of temperature increased after ageing.
- The range of combustion thermal release temperature of ageing wood was shortened. It was mainly caused by the large decrease of wood water in the process of dry and wet alternate ageing, the enhancement of cell wall pore thermal diffusion ability, and the decrease of the glass transition temperature of hemicellulose caused by the thermal effect. The main thermal energy release stage of dry and wet alternate ageing on wood combustion was the volatiles precipitation stage. After dry and wet ageing, the total thermal energy release of wood fluctuated prominently with the growth of heating rate, more than that of fresh wood, and the change of external environment disturbed the ignition process more.
- In the early stage of accelerated exothermic stage, dry and wet ageing reduced the energy barrier of wood exothermic generation. Alternate ageing of dry and wet elm had the greatest impact on the energy demand of thermal reaction in the accelerated thermal release stage. Because of the early consumption of volatiles, the influence of alternate dry and wet reaction energy ageing for different types of wood in the rapid exothermic stage was quite different.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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