# Effects of Extractives on Degradation Characteristics and VOCs Released during Wood Heat Treatment

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*Eucalyptus* was applied to investigate the influence of extractives on thermo-degradation of wood during heat treatment. Degradation characteristics, specifically the thermal degradation kinetics and volatile products during the heat treatment, were studied. A kinetic analysis was performed based on the Arrhenius equation and the time-temperature superposition principle. A devolatilization analysis was then conducted according to the chromatography identification. The results showed that the extractives facilitated the thermo-degradation and initiated the degradation at a lower temperature. An earlier degradation starting point was detected, and a lower activation energy of 65.7 kJ/mol was calculated for the non-extracted *Eucalyptus*. The VOCs collected in this research were primarily acetates, furans, terpenes, and other compounds. The non-extracted specimen released more VOCs than the extracted specimen. Compared with extracted samples, further hemicellulose degradation was identified for the non-extracted samples at the whole stage of 180 °C and a temperature-elevating period of 200 °C, as well as lignin decomposition at the temperature-holding section of 220 °C. However, only hemicellulose degradation was observed in extracted samples. This research could be helpful for the mechanism explanation of wood heat treatments and to promote the process to be more efficient and environmentally friendly.

*Keywords: Degradation characteristics; Heat treatment; Extractives; Eucalyptus*

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## INTRODUCTION

Heat treatments are eco-friendly alternatives to chemical treatments in wood preservation (Awoyemi and Jones 2011; Chu *et al*. 2019) and are typically applied to acquire modified physical properties for particular purposes, such as the dimensional stability and durability of the wood (Dosdall *et al*. 2015). The nontoxic chemical agents used during the process makes these treatments more environmentally accepted and attractive (Brosse *et al*. 2010; Poncsak *et al*. 2011). During the treatment, an inert atmosphere and a heating environment of 160 to 250 °C are created for the wood (Poncsak *et al*. 2011; Zhu *et al*. 2014). After the process, the material has experienced a certain anhydrous mass loss (Tjeerdsma and Militz 2005; Candelier *et al*. 2013a) and modified properties including decreased hygroscopicity (Hakkou *et al*. 2005), improved dimensional stability (Niemz and Bekhta 2003), darkened color (Mitsui *et al*. 2001; Chu *et al*. 2016), enhanced fungal durability (Hakkou *et al*. 2006), and weakened mechanical behavior (Welzbacher *et al*. 2007). These changed performances are attributed to the thermal degradations of the wood components, which involve a series of hydrolysis, dehydration, and decarboxylation reactions (Tjeerdsma *et al*. 1998; Singh *et al*. 2013; Willems *et al*. 2013). Consequently, a better understanding on the degradation characteristics of wood components during heat treatments provides a basis for an effective and efficient wood modification. Furthermore, in recent years, the challenges of VOCs released during heat treatments have arisen, and the VOCs emissions from wood products have attracted increasing attention relative to their impacts on environmental and human health (Hazrati *et al*. 2016; Chen *et al*. 2017). Although a lot of studies on the characterization of emissions before and after thermal medication have been reported (Pohleven *et al*. 2019), studies of the emission during wood heat treatment are relatively limited.

As a result of the degradation and volatilization of wood components during heat treatments (Gabriel *et al*. 2015), the issues regarding VOCs released from wood heat treatment call for further investigation on the degradation characteristics of wood components. So far, the thermal degradation characteristics of the lignocellulosic biomass have been studied, particularly in the high temperature zone (Fisher *et al*. 2002; Prins *et al*. 2006; Zhang and Zhang 2012). The pyrolysis mechanisms are explained by the single or combined thermal behaviors of the cellulose, hemicellulose, and lignin. The extractive behaviors are generally neglected due to their slight content, which are generally 2% to 5% (Zhang *et al*. 2007), when compared with the main components. However, the mass loss of the main components becomes small during the mild pyrolysis at low temperature heat treatments, which is typically less than 14% (Sundqvist *et al*. 2006). In this case, the content and degradation of the extractives should not be ignored anymore (Hofmann *et al*. 2013; Altgen *et al*. 2016). In addition, the influence of extractives ought to be introduced into the explanation of degradation mechanisms of treated wood. Unfortunately, reports on the effects of extractives on wood degradation characteristics during heat treatments are insufficient.

Among the studies on the degradation mechanisms, the investigation methods mainly regard two aspects: studying the chemical transformations before and after the heat treatment according to the changes in composition quantity, structure, functional groups, crystallinity, pH value of water extracts, *etc*. (Brosse *et al*. 2010; Dubey *et al*. 2011; Windeisen *et al*. 2007), or analyzing the degradation characteristics based on VOCs released during the treatment process and the mild pyrolysis kinetics (Pétrissans *et al*. 2012; Candelier *et al*. 2013c; Goli *et al*. 2014). In this study, the focus was on the latter, not only because it is characterized by high efficiency due to the rapid and simple process with less apparatuses and procedures involved, but also because it provides more information about the VOCs produced in the heat treatment.

The objective of this research was to determine the effects of extractives on the degradation characteristics and VOCs released during the wood heat treatment, mainly by investigating the kinetics and organic volatiles emissions with thermogravimetric analysis (TGA) and a gas chromatography-mass spectrometer (GC-MS). *Eucalyptus grandis* × *E. urophylla* was selected as specimens because it is one of the most important artificial forest trees in China (Deng *et al*. 2010). This research could enrich the explanation theory of degradation mechanisms during the wood heat treatment and could promote efficient and environmentally friendly applications of the *Eucalyptus grandis* × *E. urophylla*.

## EXPERIMENTAL

### Materials and Methods

*Eucalyptus* specimens

The *Eucalyptus (Eucalyptus grandis* × *E. urophylla)* used in this study was obtained as air-dried wood with a 10% to 15% moisture content and 1200 mm × 100 mm × 20 mm (L × T × R) dimension from Xianglong Forestry Co. Ltd in Lipu, Guangxi, China. The defect-free heartwood blocks cut from the same board were ground and passed through a 60-mesh sieve to obtain particles below 0.25 mm. The obtained particles were oven-dried at 103 ± 2 °C to a constant weight and then stored in a closed bottle before analysis.

*Extraction with organic solvents*

Half of the oven-dried samples were extracted in a Soxhlet extractor (Beijing Glass Group Company, Beijing, China) with a benzene/ethanol (2:1, v/v) mixture for 12 h. Each experiment contained 3 g of wood and 150 mL of solvent. Afterwards, the extracted samples were dried at 103 ± 2 °C to a constant weight and stored in a closed bottle for further experiments.

*Thermogravimetric analysis of the non-extracted and extracted samples*

The TGA was conducted by a TA instruments Q5000 thermo-gravimetric analyzer (Delaware, United States). The sample weight for every test was 8 to 10 mg, and the flow rate of the high purity nitrogen was 50 mL/min. Two steps were involved in each experiment. The first step had a heating rate of 30 °C/min, a final temperature of 100 °C, and a retention time of 10 min. The second step had a heating rate of 30 °C/min, a final temperature of 180 °C, 200 °C, or 220 °C, and a retention time of 20 min. The mass loss data developed with the time under different temperatures were used to determine the sample degradation kinetics.

*Volatile organic compound collection generated during the oven heat treatment of samples*

The heat treatment system consisted primarily of an oven to provide a heating environment, a closed aluminum heat-treatment reactor with dimensions of 22 cm × 13 cm × 6 cm to ensure a sealed condition, a temperature data logger with three triangle-distributed thermocouples under the reactor, and a computer to detect and record the reactor temperature. The VOC collection system was composed of two parts: an air inlet section and a VOC capture section. The inlet section included a flowmeter (4) to monitor the air inletting rate, two gas-washing bottles with 30% (m/m) $FeCl_2$ solution to remove the $O_2$, and a bottle of allochroic silica gel to eliminate the water vapor. This part assured an inert atmosphere for the treated samples. As shown in Fig. 1, there were also six washing bottles containing an ethanol solvent to adequately absorb the VOCs, two bottles of distilled water to gather the escaped ethanol, a flowmeter to inspect the collecting rate, three valves to control the airflow direction, and an air pump to continuously supply power to the collection system. All the bottles applied in the system were 250 mL and 150 mL $FeCl_2$ solution or ethanol solvent was used in every bottle.

Each trial run needed 23 to 27 g samples of the non-extracted or extracted samples. The temperature scheme of the treatment was based on the average temperature of the three triangle-distributed thermocouples. Once the heat treatment and collection system connections were completed, the treatment scheme started. First, the oven temperature was set to 103 °C, the control valve 14 was turned on, valves 13 and 15 were turned off, and the collection flowmeter was adjusted to 700 to 750 mL/min. The inlet flowmeter was 350 to 400 mL/min at that time due to the system resistance. The value of the collection flowmeter was not kept high to protect the particle samples from being blown away by the airflow. After the reactor temperature reached 103 °C and held for 20 min, the oven was set to the target treatment temperature 180 °C, 200 °C, or 220 °C, respectively. Meanwhile, valve 13 was turned on, valve 14 was turned off, and the flowmeter was kept at 700 to 750 mL/min. When the reactor arrived at the target temperature, valve 15 was turned on and valve 13 was turned off. After maintaining the target temperature for 30 min, the heat was stopped, value 14 was turned on, and value 15 was turned off. Once the reactor temperature had decreased to 50 to 60 °C, the reactor was taken out and the VOC collection was completed. Additionally, the same operations at 180 °C, 200 °C, and 220 °C were carried out without samples to obtain the data of control groups.

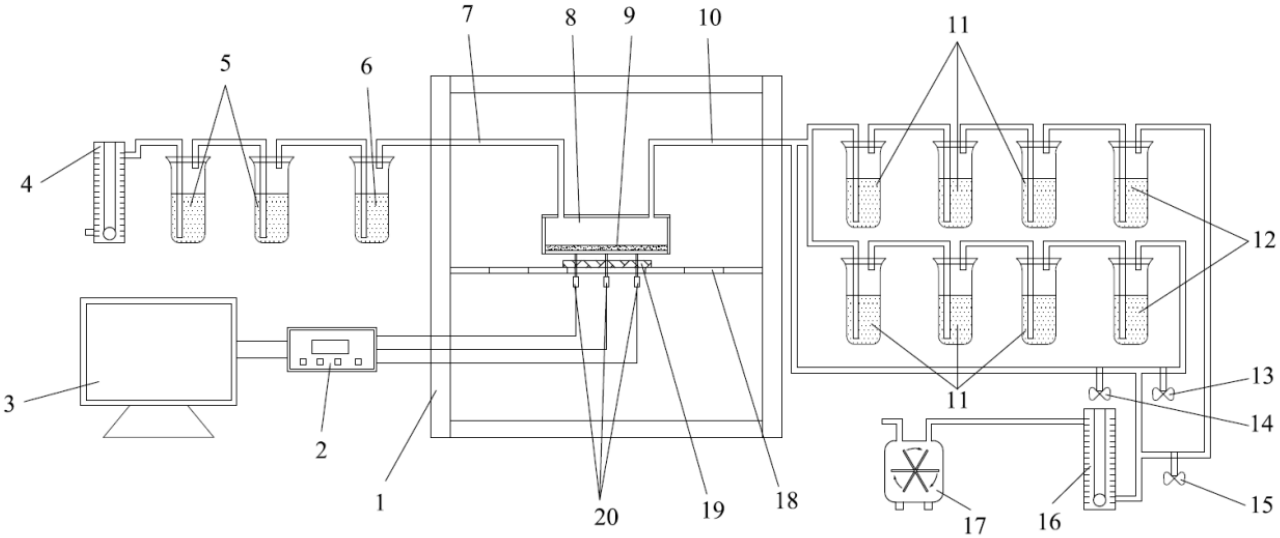


**Fig. 1.** The schematic diagram of heat treatment and VOC collection systems. (1) Oven, (2) temperature data logger, (3) computer, (4) flowmeter for inletting air, (5) gas-washing bottles with $FeCl_2$ solution, (6) gas-washing bottle with allochroic silica gel, (7) air inlet line, (8) heat treatment reactor, (9) *Eucalyptus* sawdust, (10) VOCs outlet line, (11) gas-washing bottles with ethanol, (12) gas-washing bottles with distilled water, (13)-(15) control values, (16) flowmeter for VOCs collection, (17) air pump, (18) reactor-holding device, (19) thermocouple-fixing device, and (20) thermocouples

*Gas chromatography-mass spectrometer (GC-MS) analysis of the collected VOCs*

The ethanol solutions containing VOCs from different gas-washing bottles in the same collection stage (*e.g.* temperature-elevating stage from 100 to 200 °C, or temperature-holding stage at 220 °C) were mixed together and concentrated in a rotary evaporator at 55 °C to 4 to 6 mL. Approximately 1.2 to 1.5 mL of the concentrated solutions were then anhydrated using sodium sulphate, filtered, and injected into a 2 mL chromatogram vial for GC-MS detection. The rest of the solutions were stored in a brown bottle at 4 °C. The VOC analysis was performed on a GC-MS QP 2010 (Shimadzu, Japan) with a quadrupole detector and a Rtx-5MS capillary column (30 m × 0.25 mm × 0.25 µm). Helium was used as a carrier gas with a constant flow of 1.0 mL/min. The temperature started at 50 °C for 5 min, followed by an increase of 10 °C/min until 280 °C, and remained at this temperature for 5 min. Then, 1 µL of the sample was injected, and the split ratio was 10:1. The MS spectrometer was operated in an electron ionization mode with 70 eV electron energy, and the m/z range from 33 to 450 was scanned. The components were identified on the basis of the NIST2011 and NIST2011s standard spectral library.

## RESULTS AND DISCUSSION

### Kinetic Analysis for the Non-Extracted and Extracted *Eucalyptus*

When implementing a kinetic analysis, the Arrhenius equation (Eq. 1) and an Arrhenius plot are commonly employed. The plot provides a straight line of the logarithm of determined time *versus* the treatment temperature reciprocal. This is applied to obtain the apparent activation energy by calculating its slope (Zou *et al*. 1996). However, a certain weight loss rate is needed in this method, and only one pair of time and temperature data in this weight loss rate is adopted to solve for the activation energy, which limits the accuracy of the result and the applicability of this method. In this work, the time-temperature superposition principle (TTSP) was incorporated to improve the precision of the activation energy by using more experimental data (Gillen and Clough 1989; Wise *et al*. 1995). Equation 1 is as follows,

$$k = A\exp(-\frac{E_a}{RT}) \tag{1}$$

where $k$ is the rate constant of the chemical reaction, $A$ is the frequency factor, $E_a$ is the apparent activation energy, $R$ is the gas constant, and $T$ is the absolute temperature of the reaction.

According to the TTSP, the characteristics of the materials obtained within a short time at higher temperatures are equivalent to those measured within a long time at lower temperatures. The curves of the measured value corresponding to material characteristics *vs*. the logarithm of treatment time at different temperatures can be superimposed by proper scale changes on the logarithmic time axis. The shift distance along the logarithmic time axis is referred to as the time-temperature shift factor ($a_T$), given by Eq. 2,

$$a_T = {}^{t_T}/_{t_{ref}} \tag{2}$$

where $t_{ref}$ is the test time at a reference temperature $T_{ref}$, and $t_T$ is the time required to give the same response at the test temperature $T$. Combining Eqs. 1 and 2 gives Eq. 3,

$$a_T = \exp[\frac{E_a}{R}(\frac{1}{T} - \frac{1}{T_{ref}})] \tag{3}$$

where both $T$ and $T_{ref}$ are absolute temperatures.

The apparent activation energy $E_a$ is then obtained from the slope of the $ln(a_T)$ *vs*. the $1/T$ plot. The mass changes after 100 °C with the "$\log_{10}$" of time for the non-extracted and extracted samples in different groups are presented in Fig. 2.

Figure 2 shows that the sample mass remained constant in the early stage of the heat treatment and decreased rapidly in the subsequent stage. The obvious differences of the curves under different temperatures indicate considerable effects of temperature on the degradation of both non-extracted and extracted samples. Furthermore, the extractives also made a difference in the degradation process because of the different starting points of degradation in the two samples. The non-extracted samples degraded earlier than the extracted samples, indicating their lower degradation temperature and poorer thermal stability. The same results were also found in TG curves in Fig. 3, and the differences between non-extracted and extracted samples became bigger with the increase of treatment temperature and time.

To quantify the influence of extraction on wood degradation, the apparent activation energy was calculated for both samples. According to TTSP, the data of the treatment temperature and time under different mass loss conditions should be collected prior to calculating the activation energy. This step would be conveniently achieved with the TGA, which can record the mass changes at different temperatures. In addition, the beginning of the treatment time in each group was standardized to the degradation-starting point.

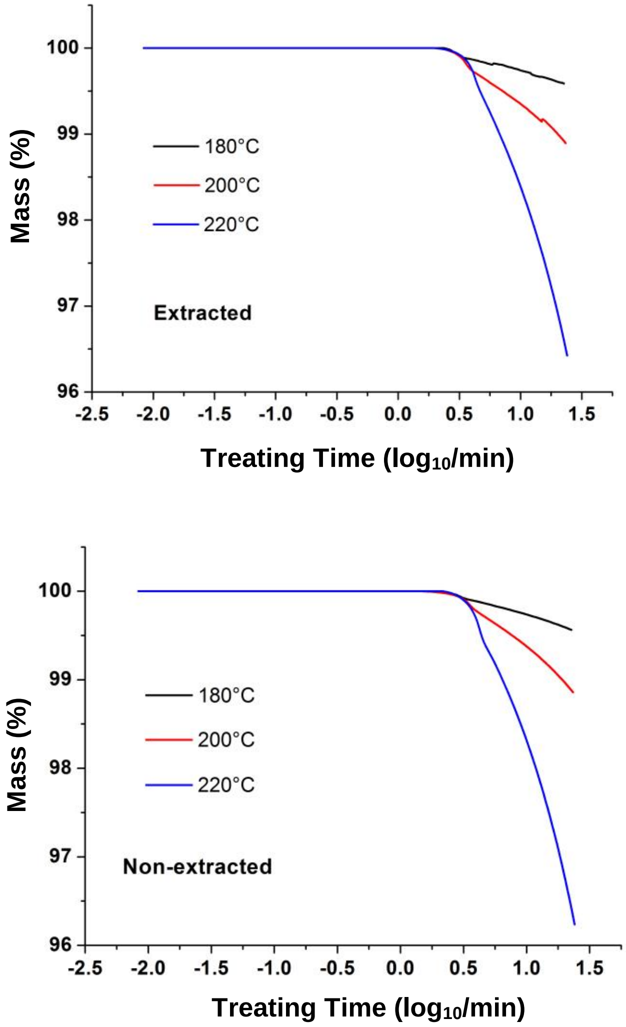


**Fig. 2.** Samples mass developing with "$\log_{10}$" of treating time after 100 °C

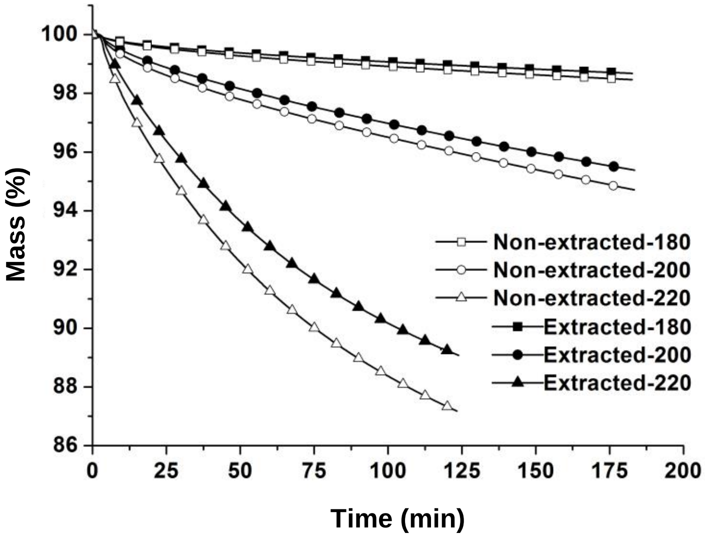


**Fig. 3.** Eucalyptus mass curves at different temperatures with or without extraction

**Table 1.** Treatment Parameters and Shift Factors for the Non-extracted *Eucalyptus*

| Mass Loss (%) | "$\log_{10}$" of Treating Time at Each Temperature (min) | | | Shift Factors for Each Temperature ($a_T$) | | |
|---|---|---|---|---|---|---|
| | 180 °C | 200 °C | 220 °C | 180 °C | 200 °C | 220 °C |
| 0.05 | -0.022 | 0.103 | -0.187 | -0.217* | 1.000 | -1.822* |
| 0.10 | 0.226 | 0.247 | -0.004 | 0.915* | 1.000 | -0.015* |
| 0.15 | 0.502 | 0.314 | 0.103 | 1.600* | 1.000 | 0.327* |
| 0.20 | 0.701 | 0.368 | 0.169 | 1.905 | 1.000 | 0.459 |
| 0.25 | 0.870 | 0.443 | 0.215 | 1.963 | 1.000 | 0.486 |
| 0.30 | 1.014 | 0.521 | 0.251 | 1.947 | 1.000 | 0.482 |
| 0.35 | 1.136 | 0.596 | 0.281 | 1.907 | 1.000 | 0.471 |
| 0.40 | 1.136 | 0.665 | 0.303 | 1.708* | 1.000 | 0.455 |
| 0.45 | -- | 0.732 | 0.324 | -- | 1.000 | 0.442 |
| 0.50 | -- | 0.792 | 0.346 | -- | 1.000 | 0.436 |
| 0.55 | -- | 0.852 | 0.370 | -- | 1.000 | 0.434 |
| 0.60 | -- | 0.907 | 0.398 | -- | 1.000 | 0.439 |
| 0.65 | -- | 0.957 | 0.430 | -- | 1.000 | 0.449 |
| 0.70 | -- | 1.006 | 0.465 | -- | 1.000 | 0.462 |
| 0.75 | -- | 1.052 | 0.496 | -- | 1.000 | 0.472 |
| 0.80 | -- | 1.094 | 0.526 | -- | 1.000 | 0.481 |
| 0.85 | -- | 1.136 | 0.554 | -- | 1.000 | 0.488 |
| 0.90 | -- | 1.175 | 0.580 | -- | 1.000 | 0.494 |
| 0.95 | -- | 1.212 | 0.606 | -- | 1.000 | 0.500 |
| 1.00 | -- | 1.247 | 0.629 | -- | 1.000 | 0.505 |
| | | | Average $a_T$ | 1.931 | 1.000 | 0.468 |

*Removed data when calculating the average $a_T$ to obtain a higher precision

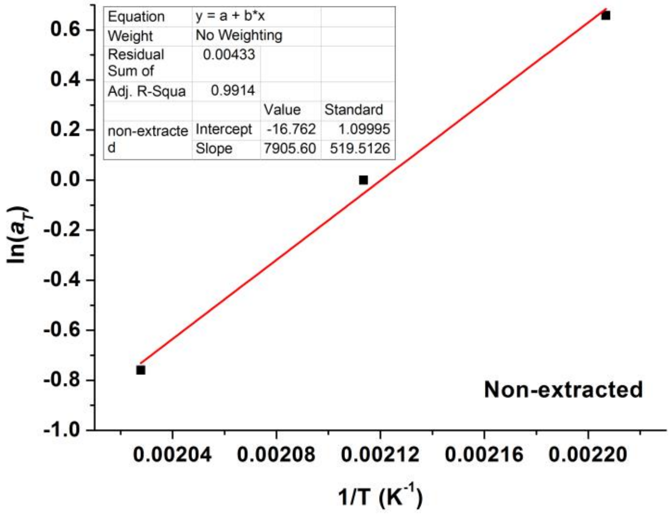
**Table 2.** Treatment Parameters and Shift Factors for the Extracted *Eucalyptus*

| Mass Loss (%) | "$\log_{10}$" of Treating Time at Each Temperature (min) | | | Shift Factors for Each Temperature ($a_T$) | | |
|---|---|---|---|---|---|---|
| | 180 °C | 200 °C | 220 °C | 180 °C | 200 °C | 220 °C |
| 0.05 | -0.294 | -0.120 | -0.030 | 2.446 | 1.000 | 0.249* |
| 0.10 | -0.050 | 0.058 | 0.133 | -0.865* | 1.000 | 2.311* |
| 0.15 | 0.336 | 0.146 | 0.217 | 2.298 | 1.000 | 1.488* |
| 0.20 | 0.693 | 0.202 | 0.269 | 3.434* | 1.000 | 1.333* |
| 0.25 | 0.861 | 0.271 | 0.306 | 3.176* | 1.000 | 1.130* |
| 0.30 | 0.993 | 0.368 | 0.332 | 2.700 | 1.000 | 0.903* |
| 0.35 | 1.149 | 0.465 | 0.355 | 2.471 | 1.000 | 0.764* |
| 0.40 | 1.270 | 0.547 | 0.377 | 2.322 | 1.000 | 0.689* |
| 0.45 | -- | 0.630 | 0.401 | -- | 1.000 | 0.636* |
| 0.50 | -- | 0.705 | 0.427 | -- | 1.000 | 0.606 |
| 0.55 | -- | 0.773 | 0.455 | -- | 1.000 | 0.589 |
| 0.60 | -- | 0.838 | 0.483 | -- | 1.000 | 0.576 |
| 0.65 | -- | 0.900 | 0.510 | -- | 1.000 | 0.566 |
| 0.70 | -- | 0.958 | 0.536 | -- | 1.000 | 0.559 |
| 0.75 | -- | 1.006 | 0.562 | -- | 1.000 | 0.559 |
| 0.80 | -- | 1.055 | 0.586 | -- | 1.000 | 0.556 |
| 0.85 | -- | 1.102 | 0.610 | -- | 1.000 | 0.554 |
| 0.90 | -- | 1.181 | 0.633 | -- | 1.000 | 0.537 |
| 0.95 | -- | 1.221 | 0.656 | -- | 1.000 | 0.537 |
| 1.00 | -- | 1.256 | 0.677 | -- | 1.000 | 0.539 |
| | | | Average $a_T$ | 2.447 | 1.000 | 0.562 |

*Removed data when calculating the average $a_T$ to obtain a higher precision

The temperature of 200 °C was chosen as the reference temperature ($T_{ref}$) because it was in the middle of the temperature range used for the heat treatments. Then, the time-temperature shift factor ($a_T$) could be obtained based on the Eq. 2. All collected treatment data and shift factors obtained from Eq. 2 for two different samples are displayed in Tables 1 and 2.

The logarithm of $a_T$ is plotted *versus* the temperature reciprocal in Fig. 4. After linear approximation, the apparent activation energies, 65.7 kJ/mol and 68.5 kJ/mol for the non-extracted and extracted samples, respectively were calculated on the basis of Eq. 3. These values were consistent with the range of 20.8 to 78.45 kJ/mol reported for the majority of hardwood species (Herrera *et al*. 1986) and that of 56 to 170 kJ/mol summarized by Branca and Blasi (2003). Thus, these activation energies for the *Eucalyptus* samples were reasonable. The value of the non-extracted sample was lower than that of the extracted sample, which indicates the extractives could have been an accelerating effect on the wood component degradation. The VOCs released during the heat treatment in different temperatures were analyzed to further investigate the influence of extractives on the degradation characteristics.



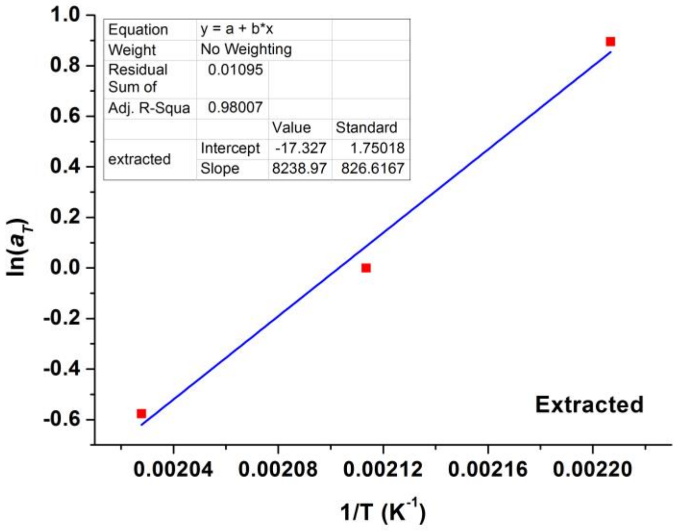


**Fig. 4.** Arrhenius plots of ln($a_T$) *versus* 1/$T$ for non-extracted and extracted *Eucalyptus*

## Devolatilization Analysis for the Non-Extracted and Extracted Samples

Many VOCs are produced and released during wood heat treatments. These compounds are mainly derived from volatile extractives and evaporable byproducts formed from the degradation of wood components (Lekounougou and Kocaefe 2012; Candelier *et al*. 2013b). The devolatilization analysis is of great importance to better understand the wood thermo degradation mechanisms as well as controlling hazardous substance emissions in VOCs. The VOCs collected during the heat treatment of the non-extracted and extracted samples were identified with GC-MS. The results revealed that the chromatographic peaks mainly located in the former 20 min of the obtained chromatograms. Thus, these parts in chromatograms were selected to illustrate the VOCs identification in Figs. 5 and 6.

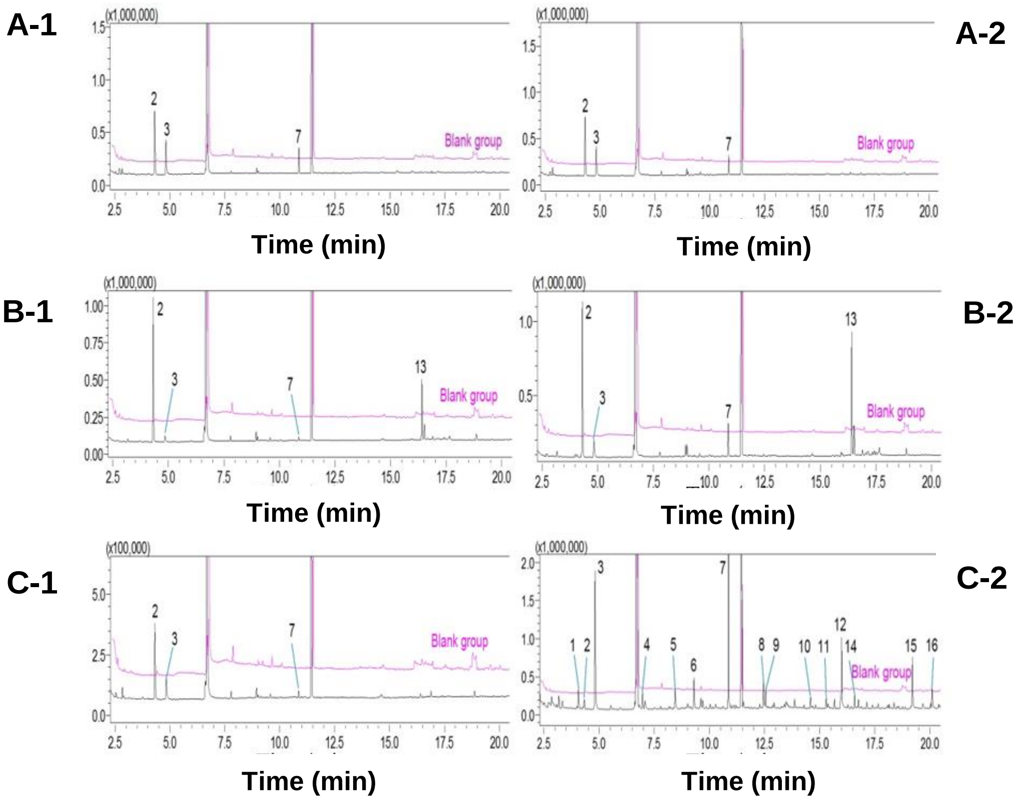


**Fig. 5.** Chromatograms of non-extracted samples in different temperatures and collection stages (A) 180 °C, (B) 200 °C, (C) 220 °C, (1) temperature-elevating stage; (2) temperature-holding stage

To compare the differences of VOCs released from different conditions, Table 3 summarizes the identified compounds in each stage and their retention time. These organic volatiles generated from the *Eucalyptus* heat treatment were primarily acetates (diethoxymethyl acetate, butyl acetate, ethyl diethoxyacetate, isobutyl acetoacetate), furans (furfural, 5-methyl-furfural, furfural diethyl acetal), phenolics (syringol, vanillin, syringaldehyde, coniferaldehyde), terpenes (α-cedrene) and other compounds (2,2-diethyl-3-methyl-oxazolidine, N-vinyl-2-pyrrolidinone, 2-methyl-2-hydroxyhexane, 1,2,4-trimethoxybenzene). These released organic volatiles were similar to the results reported in the references (Graf *et al*. 2005; Candelier *et al*. 2013c). The difference was that acetic acid was identified in the references while acetates were determined in this research. This may have been due to secondary reactions (Masih *et al*. 2017; Marć *et al*. 2018) and degradation of fatty acid esters in the extractives (Korus *et al*. 2019).

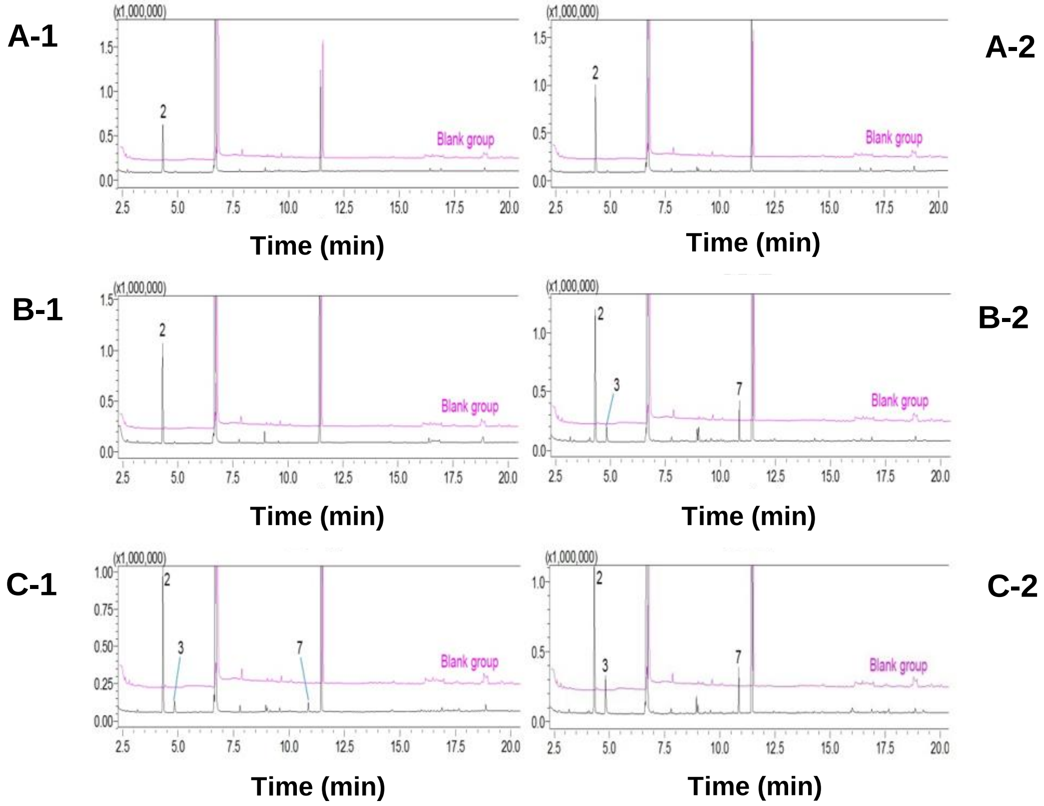


**Fig. 6.** Chromatograms of extracted samples in different temperatures and collection stages (A) 180 °C, (B) 200 °C, (C) 220 °C, (1) temperature-elevating stage, and (2) temperature-holding stage

The collected compounds from the non-extracted samples, which showed all the categories mentioned above, were more abundant than those for the extracted specimens, which only contained acetates and furans. In addition, a higher treatment temperature led to more plentiful compound types in both the extracted and non-extracted samples, which demonstrated the more intensive decomposition of wood components with increasing temperature. The VOCs released during the temperature-elevating and temperature-holding stages were consistent with each other for most of the treatment conditions. However, the variation between the two stages appeared in the 220 °C process for the non-extracted specimens and 200 °C treatment for the extracted samples. At these two temperatures, the temperature-holding stage displayed more VOCs than the temperature-elevating stage. Additionally, the increase in non-extracted samples was more than that in extracted samples. Therefore, according to the different emitting status of the non-extracted and extracted *Eucalyptus* in different temperatures and stages, it could be concluded that the VOCs emission during the heat treatment was affected by the extractives, temperature, and treating time. In general, although the extractives only accounted for a small part in the wood components, they made the samples generate more organic compounds during the heat treatment compared to the extracted specimens at the same condition. It was not only because the degradation of extractives themselves, but may also result from the interaction between extractives and primary wood components.

**Table 3.** Identified VOCs and Their Retention Time during Each Treatment for Non-extracted and Extracted *Eucalyptus*

| | VOCs | Retention Time for Non-extracted *Eucalyptus* | | | | | | Retention Time for Extracted *Eucalyptus* | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | A-1 | A-2 | B-1 | B-2 | C-1 | C-2 | A-1 | A-2 | B-1 | B-2 | C-1 | C-2 |
| 1 | Diethoxymethyl Acetate | -- | -- | -- | -- | -- | 4.058 | -- | -- | -- | -- | -- | -- |
| 2 | Butyl Acetate | 4.321 | 4.321 | 4.317 | 4.314 | 4.318 | 4.321 | 4.321 | 4.318 | 4.309 | 4.308 | 4.317 | 4.317 |
| 3 | Furfural | 4.827 | 4.829 | 4.850 | 4.835 | 4.833 | 4.808 | -- | -- | -- | 4.825 | 4.842 | 4.825 |
| 4 | Ethyl Diethoxyacetate | -- | -- | -- | -- | -- | 6.697 | -- | -- | -- | -- | -- | -- |
| 5 | 5-Methyl-furfural | -- | -- | -- | -- | -- | 8.442 | -- | -- | -- | -- | -- | -- |
| 6 | 2,2-Diethyl-3-methyl-oxazolidine | -- | -- | -- | -- | -- | 9.300 | -- | -- | -- | -- | -- | -- |
| 7 | Furfural Diethyl Acetal | 10.867 | 10.868 | 10.867 | 10.865 | 10.864 | 10.867 | -- | -- | -- | 10.858 | 10.867 | 10.867 |
| 8 | N-Vinyl-2-pyrrolidinone | -- | -- | -- | -- | -- | 12.450 | -- | -- | -- | -- | -- | -- |
| 9 | 2-Methyl-2-hydroxyhexane | -- | -- | -- | -- | -- | 12.550 | -- | -- | -- | -- | -- | -- |
| 10 | Isobutyl Acetoacetate | -- | -- | -- | -- | -- | 14.583 | -- | -- | -- | -- | -- | -- |
| 11 | Syringol | -- | -- | -- | -- | -- | 15.292 | -- | -- | -- | -- | -- | -- |
| 12 | Vanillin | -- | -- | -- | -- | -- | 15.992 | -- | -- | -- | -- | -- | -- |
| 13 | $\alpha$-Cedrene | -- | -- | 16.408 | 16.409 | -- | -- | -- | -- | -- | -- | -- | -- |
| 14 | 1,2,4-Trimethoxybenzene | -- | -- | -- | -- | -- | 16.583 | -- | -- | -- | -- | -- | -- |
| 15 | Syringaldehyde | -- | -- | -- | -- | -- | 19.200 | -- | -- | -- | -- | -- | -- |
| 16 | Coniferaldehyde | -- | -- | -- | -- | -- | 20.100 | -- | -- | -- | -- | -- | -- |

Note: (A) 180 °C, (B) 200 °C, (C) 220 °C, (1) temperature-elevating stage, and (2) temperature-holding stage

Wood is primarily composed of three polymeric components: cellulose, hemicellulose, and lignin. Affected by the heated environment, these wood components transform through a series of hydrolysis, dehydration, and decarboxylation reactions during the heat treatment process (Tjeerdsma *et al*. 1998; Singh *et al*. 2013; Willems *et al*. 2013). Hemicellulose is reported to be the most sensitive component to the thermal and first degrades (Boonstra and Tjeerdsma 2006; Esteves *et al*. 2011) with the cleavage of the acetyl groups leading to the formation of carbonic acids, mainly acetic acid (Dietrichs *et al*. 1978; Bourgois and Guyonnet 1988). Catalyzed by the acids, the hemicellulose is further hydrolysed into oligomeric and monomeric structures (Bobleter and Binder 1980; Carrasco and Roy 1992), which will be subsequently dehydrated to aldehydes such as furfural and methylfurfural (Burtscher *et al*. 1987; Kaar *et al*. 1991; Ellis and Paszner 1994). Meanwhile, production parts derived from the hemicellulose degradation are released into the heat treatment environment, and the others can also become available to further depolymerize the cellulose and lignin (Boonstra and Tjeerdsma 2006). The levoglucosan and phenolics are often considered as the main product of cellulose and lignin thermal degradation (Esteves *et al*. 2007; Windeisen *et al*. 2007).

During the *Eucalyptus* heat treatment in this research, the butyl acetate was collected during all treatment conditions, most likely corresponding to the hemicellulose degradation and the secondary reactions of acetic acid. During the 180 °C treatment, only butyl acetate was identified in the extracted samples. Furfural and furfural diethyl acetal were determined in the non-extracted samples, which indicated a larger degree of hemicellulose degradation. When the temperature was elevated to 200 °C, the two furans were detected in both of the two specimen. However, they did not emerge until the temperature-holding period for the extracted group. When 220 °C was reached, the VOCs in each condition involved the two furans, whereas other compounds showed during the temperature-holding stage of the non-extracted samples, including furans, acetates, and phenolics. Although the absence of levoglucosan indicated a relatively high stability of cellulose in this temperature range, the appearance of phenolics could have meant that the hemicellulose and the lignin were attacked by the heat treatment. All these phenomena confirmed that the extractives facilitated the component degradation of the *Eucalyptus* during the heat treatment. These results were consistent with the lower activation energy calculated for the non-extracted *Eucalyptus* and in harmony with the published judgments that the removal of extractives improves the thermal stability of the wood (Shebani *et al*. 2008) and higher extractive contents leads to lower thermal stability (Poletto 2016). Except for the disintegration of extractives, this acceleration of degradation can be explained by the presence of acid substances such as resin acids, fatty acids, and phenolic acids in the extractives (Ishida *et al*. 2007; He *et al*. 2013; Chen *et al*. 2014). These acid substances catalyzed the decomposition of the natural polymer and resulted in a lower degradation temperature.

## CONCLUSIONS

1. The presence of extractives in the wood had an obvious effect on the degradation characteristics during the heat treatment of *Eucalyptus grandis* × *E. urophylla*. The non-extracted *Eucalyptus* had a lower apparent activation energy of 65.7 kJ/mol compared with the 68.5 kJ/mol for extracted sample.

2. The VOCs collected in this research were primarily acetates, furans, terpenes, and other compounds. The VOCs collected in non-extracted group were much more than those in the extracted samples, which means extraction could be a useful method to decrease the release of VOCs in heat treatments.
3. The butyl acetate was detected for all treatment conditions, and revealed revealed significant degradation of hemicellulose during each process. Compared with the same stage of the extracted specimens, more organic compounds such as furans, terpenes, and phenolics were identified for the non-extracted samples at the whole stage of 180 °C and 200 °C, and temperature-holding section of 220 °C, indicating the decomposition of extractives and further degradation of hemicellulose and lignin during these periods.
4. The kinetic analysis and the devolatilization analysis for the non-extracted and extracted *Eucalyptus* both demonstrated that the extractives promoted the wood thermo-degradation and initiated the degradation at a lower temperature.

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