

# BENCH-SCALE STUDIES ON WOOD PYROLYSIS UNDER DIFFERENT ENVIRONMENTS

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## ABSTRACT

Wood pyrolysis under a real fire was studied by thermogravimetric analysis and fir particles were selected as the testing sample. The consumption and supply of oxygen during pyrolysis process was considered. Pyrolysis from ambient to 700°C under normal steady environment was studied as well. Consumption of oxygen in the pyrolysis process would have an obvious effect on the mass loss rate and heat released. The final residue yield depended on the atmosphere in the second stage, lying from about 375 to 500°C. With the supply of air, the oxidation of gaseous product and char gave out much heat, and finally reached a low residue yield. When the heat source was removed during pyrolysis and then put in again, water evaporated before 150°C. The samples began to decompose at a lower temperature.

**KEYWORDS:** Pyrolysis, Atmosphere, Switching, Mass loss, Oxidation

## INTRODUCTION

Pyrolysis is the first step of unwanted fire hazards<sup>1</sup>. Ignition and consequent flame spread over combustibles depend on supplying volatiles due to pyrolysis. The mass loss rate is related to the heat generated. Thus, it is very useful to understand the pyrolysis behavior of fuels. In fire safety, pyrolysis almost refers to the thermal degradation of solid fuels due to external heating<sup>2</sup>. Wood is the charring material commonly used in buildings, as large slabs, furniture, partitions, doors and others. Moreover, in forest fires, wood is the dominant fuel. As a substantial element of fuel load in fires, wood has been of great interest in the past decades.

A number of studies had been carried out on pyrolysis of different wood species by thermogravimetric analysis<sup>3-14</sup>. Kinetic parameters were deduced at controlled conditions. Much research had been carried out on wood pyrolysis in N<sub>2</sub> atmosphere, and various kinetic models were proposed<sup>3-5</sup>. Isothermal and dynamic experiments of several common timbers were done by Momoh et al.<sup>6</sup> and Bilbao et al.<sup>7</sup> under atmospheric conditions. Two well-defined pyrolysis stages were observed. Kinetics of thermal decomposition of four wood species in inert and oxidizing atmospheres of different O<sub>2</sub> concentrations was studied by Cordero et al.<sup>8</sup> Kinetic modeling illustrated that the whole process could be represented in two stages. Fang et al.<sup>9</sup> had studied the pyrolysis and combustion of wood under different O<sub>2</sub> concentrations by using TG-FTIR analysis, and divided the whole process into four steps. More researches focused on pyrolysis of three components of wood, those are cellulose, hemicellulose and lignin<sup>10-14</sup>. All the studies were performed at some fixed conditions, and well-fitted kinetic parameters were obtained.

However, a real fire is affected by many conditions such as environment, geometrical configurations and others. For example, a fatal fire started by smoking in bed broke out in a hotel in Harbin in 1985. At the beginning, just the bedding smoldered. Choking on an acrid smoke, the guest woke up and got away. Due to air entrance from the door and sufficient oxygen supply, the smolder became flaming combustion. Fire spread quickly and flashover occurred in a short time. In this case, O<sub>2</sub> concentration decreased before opening the door and increased gradually after that. In another

incident, a disastrous forest fire occurred in Daxinganling of Heilongjiang province in 1987, lasting 28 days. Initially, the five points of origin were extinguished or controlled. Unfortunately, the controlled fire developed greatly due to the strong wind. In that case, fuels might be cooled down during pyrolysis process. The temperature rose up again when a new heat source appeared. Hence, a simple heating procedure and fixed atmospheric condition cannot reflect the complex environment in a real fire. To study pyrolysis more realistically, the fire conditions have to be defined.

In this paper, wood pyrolysis under a real fire was studied. Environments of the scenarios identified above were simplified and simulated in a thermogravimetric analyzer. This was achieved by operating three conditions:

- Oxygen is consumed at a temperature, and the atmosphere changes from air to N<sub>2</sub>.
- The supply of air makes the atmosphere change from N<sub>2</sub> to air.
- The appearance of new heat source restarts the pyrolysis of cooled fuels.

## MATERIALS AND METHODS

Fir particles with a diameter range of 0 to 100  $\mu$ m were selected as the testing sample. Before the experiments, the sample was dried at the temperature of 333K for 2 hours. The proximate and elemental analysis of fir particles is shown in Table 1. The contents of volatile, fixed carbon, ash and moisture could be obtained.

**TABLE 1.** Proximate and elemental analysis of fir particles

| Wood | M <sub>ad</sub> % | A <sub>ad</sub> % | V <sub>ad</sub> % | FC <sub>ad</sub> % | C <sub>ad</sub> % | H <sub>ad</sub> % | N <sub>ad</sub> % | S <sub>ad</sub> % | O <sub>ad</sub> % | Q <sub>bad</sub> (J/g) |
|------|-------------------|-------------------|-------------------|--------------------|-------------------|-------------------|-------------------|-------------------|-------------------|------------------------|
| Fir  | 9.54              | 3.19              | 74.21             | 13.06              | 44.92             | 6.01              | 0.35              | 0.14              | 35.85             | 18129.7                |

Thermogravimetric analysis was performed on a Mettler-Toledo TGA/SDTA851e thermo-balance. All the linear temperature increase from ambient to 700°C was carried out at a heating rate of 20 °C/min. Nitrogen of purity over 99.99% at a steady flow of 40 ml/min was selected as the carrier gas. A quantity of fir particles about 5 mg was used in each experiment to minimize diffusional effects.

TGA experiments were carried out under the following defined conditions:

Condition 1: Supply normal air at atmospheric condition, and then cut off air supply at a predetermined temperature (at 200°C, 300°C, 400°C or 500°C) and supply pure nitrogen.

Condition 2: Supply pure nitrogen only, then cut off nitrogen supply at the predetermined temperatures and supply normal air.

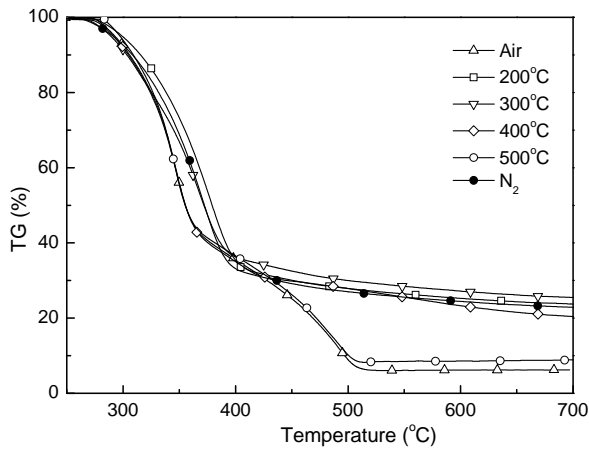
Condition 3: Under atmospheric air, the samples are heated up to the predetermined temperatures. Remove the heat source and cool down the samples to 50°C, then turn on again to 700°C.

Pyrolysis from ambient to 700°C under normal steady environment was studied as well.

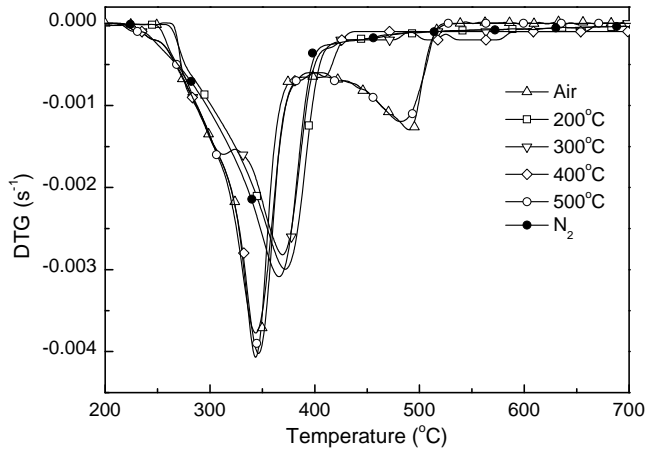
## RESULTS AND DISCUSSION

Condition 1: Atmospheric change from Air to N<sub>2</sub>

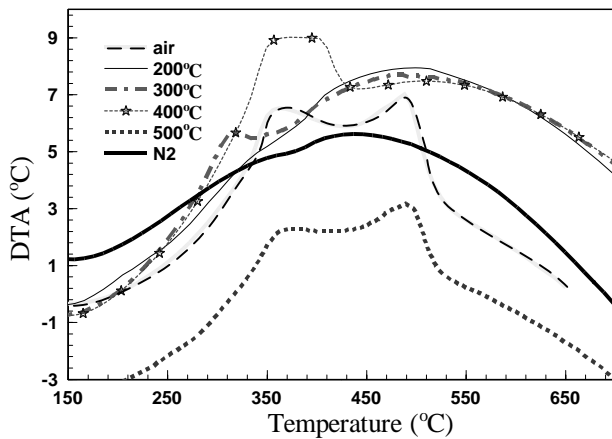
TG (thermogravimetry), DTG (differential thermogravimetry) and DTA (differential thermal analysis) curves for atmospheric change from air to N<sub>2</sub> are shown in Figs. 1 to 3. The six atmospheric settings are: air, N<sub>2</sub>, change from air to N<sub>2</sub> at 200°C, 300°C, 400°C or 500°C.



**FIGURE 1.** TG curves of fir pyrolysis under different environments



**FIGURE 2.** DTG curves of fir pyrolysis under different environments



**FIGURE 3.** DTA curves of fir pyrolysis under different environments

As shown in Figs. 1 and 2, in pure nitrogen, the pyrolysis of fir particles occurred in a wide temperature range, corresponding to one single mass loss apex in the DTG curve. There were two stages of pyrolysis in the presence of air. In the first stage, ignition might begin in gaseous phase

without affecting the char yield. The second stage would give char oxidation. The main pyrolysis stage lay from 200 to 500°C under both atmospheres. Compared to the pyrolysis in air, the weight loss of the first stage in the atmosphere of N<sub>2</sub> occurred at higher temperature, and the temperature range was wider. Similarly, it was reported that the maximum heat release rate of samples shifted to lower temperature with the increase in oxygen concentration<sup>15</sup>.

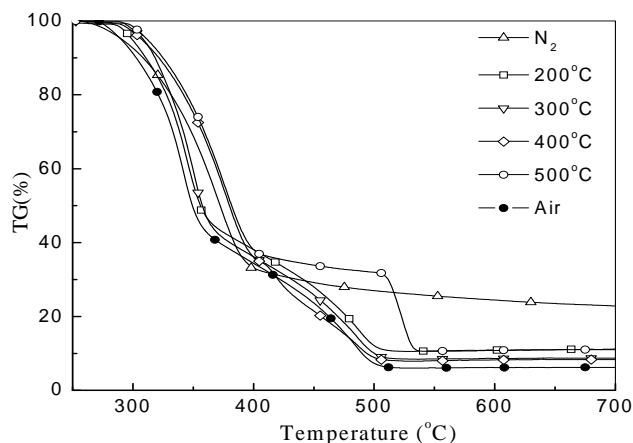
When changing the atmosphere from air to N<sub>2</sub> at 500°C, the pyrolysis process was quite similar to that under air. When changing at 200°C, it was consistent with that under N<sub>2</sub>. It was concluded that the variety of atmosphere before 200°C or after 500°C would not influence the weight loss obviously. Before changing from air to N<sub>2</sub> at 300°C, the first pyrolysis stage began in air. When 20°C after the change of atmosphere, the weight loss curve deviated from the original one and approached that in N<sub>2</sub> gradually. The final pyrolysis trend was consistent with that in N<sub>2</sub> in the whole process. When switching the atmosphere at 400°C, fir particles underwent the first pyrolysis stage in air, and then pyrolyzed with the trend in N<sub>2</sub> immediately. Based on the analysis above, variation of atmosphere in the first stage had slight effects on the final mass loss. The final residue yield depended on the atmosphere in the second stage, lying from about 375 to 500°C. Ignition might happen in the first stage in air. According to the weak effect to the char yield, in the first stage, ignition might occur in gaseous phase. The second weight loss stage in air atmosphere was attributed to the oxidation of char, corresponding to the second apex in DTG curve. When switching from air to N<sub>2</sub> at 500°C, the residue was much less than the others because of the char oxidation.

Two apexes appeared in the DTG curve when changing from air to N<sub>2</sub> at 500°C. Both were at the same temperatures with that in air. All the other DTG curves had only one apex due to the absence of air after 400°C. When switching the atmosphere at 200°C, the position of the apex was close to that in N<sub>2</sub>. When changing at 300°C or 400°C, the apexes appeared between the first apex in air and that in N<sub>2</sub>. Thus, it was illustrated that switching of air to N<sub>2</sub> in the pyrolysis process would have an obvious effect on the mass loss rate and heat released.

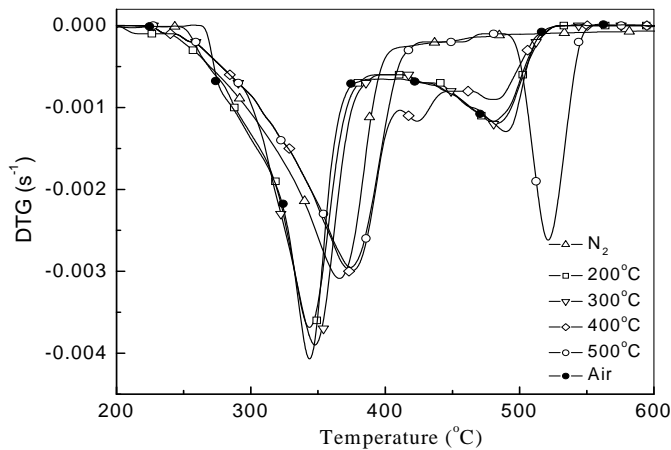
DTA curves in Fig. 3 showed the endothermic or exothermic processes in different pyrolysis conditions. The pattern of DTA curve in air was quite different from that in N<sub>2</sub>. Two obvious exothermic apexes formed in the atmosphere of air, while in N<sub>2</sub> the curve was much smoother. The apex in the temperature range of 450 to 540°C was attributed to char oxidation. The patterns of the curves in air and changing atmosphere at 500°C were similar, with numerical difference due to the variety of experimental base. Same explanation applies to other curves.

#### Condition 2: Atmospheric change from N<sub>2</sub> to Air

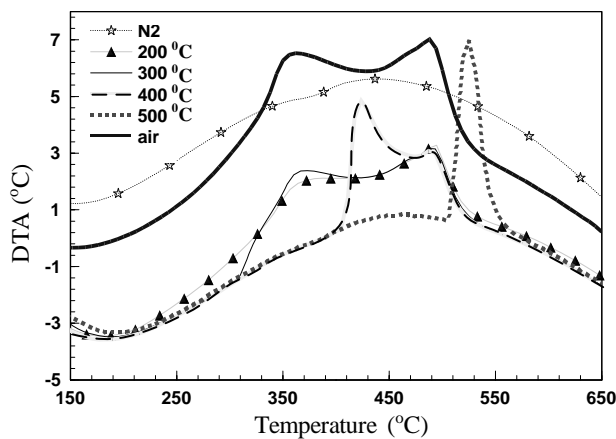
TG, DTG and DTA curves for atmospheric change from N<sub>2</sub> to air are shown in Figs. 4 to 6. The six atmospheric settings are: N<sub>2</sub>, air, change from N<sub>2</sub> to air at 200°C, 300°C, 400°C or 500°C.



**FIGURE 4.** TG curves of fir pyrolysis under different environments



**FIGURE 5.** DTG curves of fir pyrolysis under different environments



**FIGURE 6.** DTA curves of fir pyrolysis under different environments

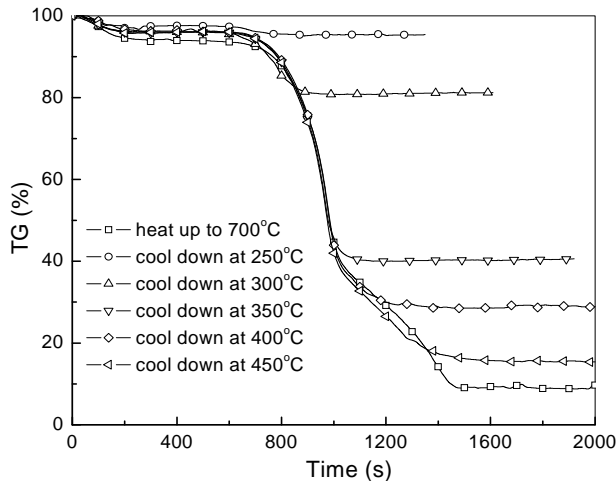
When changing from  $N_2$  to air at different temperatures, the final residue yield was almost the same. The initial atmosphere would not affect the final mass loss. With the supply of air, the oxidation of gaseous product and char gave out much heat, resulting in the relevant apexes in the DTA curves.

As shown in Figs. 4 and 5, when changing from  $N_2$  to air at  $200^\circ\text{C}$ , the pyrolysis of fir particles was similar to that in air all the time. When changing from  $N_2$  to air at  $300^\circ\text{C}$ , the weight loss curve began to approach that in  $N_2$  gradually  $20^\circ\text{C}$  after the change. Under the atmospheric change from  $N_2$  to air at  $400^\circ\text{C}$ , the weight loss became intensive immediately after the change, and a sunken trend appeared in the TG and DTG curves. The sudden oxidation reaction resulted in the increase of mass loss rate. And the final residue yield was the same as that in air. When switching at  $500^\circ\text{C}$ , the mass loss rate increased sharply, and reached the final residue yield at about  $530^\circ\text{C}$ . It is obvious that the initial atmosphere would not affect the final weight loss, as long as supplying oxygen finally.

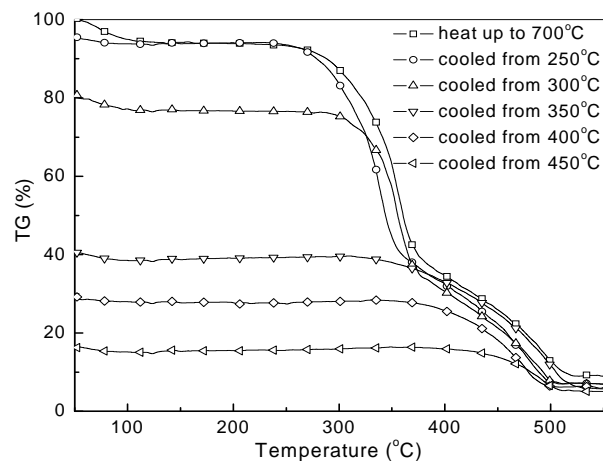
Fig. 6 showed two upward apexes in the DTA curve of fir pyrolysis in air. The pattern of apexes when switching atmosphere at  $200^\circ\text{C}$  was the same. When switching from  $N_2$  to air at  $300^\circ\text{C}$ ,  $400^\circ\text{C}$  or  $500^\circ\text{C}$ , the upward exothermic apexes appeared immediately after the change of atmosphere. Especially the apex in DTA curve of switching at  $500^\circ\text{C}$  was quite sharp, due to large amount of heat released from char oxidation.

### Condition 3: Restart pyrolysis after cooling down

Fig. 7 showed the pyrolysis curves when heated up to predetermined temperatures and then cooled down. At the beginning of the cooling process, the mass loss of fir continued for a short time and then kept constant. As shown in Fig. 8, when the heat source was put in again, water evaporated before 150°C. It is considered to be partly crystallization water, and partly condensate in the interior of sample while cooling. The samples began to decompose at a lower temperature when reheated. For example, samples cooled from 350°C restarted to pyrolyze at 310°C. For samples cooled from 450°C, the mass loss began at 370°C. It might be explained by the occurrence of mass loss in a temperature range, and the release of volatiles persisting for some time. However, the final mass loss was almost the same.



**FIGURE 7.** TG curves of fir pyrolysis when cooled at different temperatures



**FIGURE 8.** TG curves of fir pyrolysis when reheated

## CONCLUSIONS

Wood pyrolysis under a real fire at different atmospheric settings was studied. Cases of changing atmosphere during pyrolysis, and putting in the heat source again for the cooled fuels were considered. The following conclusions can be drawn:

- When switching from air to N<sub>2</sub>, variation of atmosphere in the first pyrolysis stage lying from 200 to 375°C had slight effects on the final mass loss. The final residue yield depended on the

atmosphere in the second stage, lying from about 375 to 500°C. Switching of air to N<sub>2</sub> during the pyrolysis process would have an obvious effect on the mass loss rate and heat released.

- When switching from N<sub>2</sub> to air, the initial atmosphere would not affect the final mass loss. With the supply of air, the oxidation of gaseous product and char gave out much heat, resulting in the relevant apexes in the DTA curves.
- When the heat source was removed during pyrolysis, the mass loss of fir continued for a short time while cooling. When the heat source was put in again, the samples began to decompose at a lower temperature. However, the final mass loss was almost the same.

In a real fire the thermal intensity and the oxygen concentration are both variable. The actual situation could not be simulated exactly by thermogravimetric analysis. However, the simplified experiments in this paper could mainly reflect the pyrolysis behavior of wood and the effect of atmosphere change.

With the presence of oxygen, the mass loss rate was relatively higher and occurred at lower temperature. The volatiles were released quickly. Gaseous combustion might happen before 400°C. In a real fire oxygen was most consumed by the combustion at the surface of char above 400°C. For conditions of the hotel fire presented in this paper, smoldering occurred due to the limited supply of oxygen, and the solid was subjected to self-heating. When the oxygen was exhausted below 400°C, just gaseous oxidation reaction occurred. Otherwise, the surface oxidation of char gave out much heat and caused further thermal degradation of neighbouring layer of combustible materials. With the exhaustion of oxygen, the oxidation reaction would finally stop. Ventilation was the key factor in this case. Supply of air induced the conversion of smoldering into flame combustion.

For conditions of the forest fire presented in this paper, the cooled materials during pyrolysis process were more liable to decompose when subjected to a new heat source. As a result the mass loss rate, as well as the amount of volatile and heat released were slightly higher. All these factors were beneficial to the development of a fire.

## ACKNOWLEDGEMENTS

The project is funded by the Joint Supervision of PhD Students with Zhejiang University on the project “Pyrolysis, Ignition and Combustion of Different Combustibles in Buildings” with PolyU account number: G-U227.

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