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## **Thermo-gravimetric analysis as a tool for the optimisation of wood heat treatment parameters**

Vincent Repellin<sup>1</sup>, Alexandre Govin<sup>1</sup> and René Guyonnet<sup>1</sup>

<sup>1</sup>Department of material engineering, Centre SPIN, Ecole des Mines de Saint Etienne, 158, Cours Fauriel, 42023 Saint Etienne, France

**Keywords:** heat treatment; thermo-gravimetric analysis ; wood pyrolysis; time temperature equivalence.

### **ABSTRACT**

Retification is a heat treatment that decreases the swelling of wood and increases its resistance to fungal attack. It consists in a mild pyrolysis of wood (180°C-260°C) that takes place in a non oxidative atmosphere (nitrogen). The industrial development of retification requires optimisation of the treatment temperature and duration. In order to enhance the homogeneity of temperature in the furnace, and to avoid exothermic reaction, low temperatures seem to be preferable to high temperature. On the contrary, duration and temperature of treatment have to be high enough to provide good biological resistance and stabilization to the wood. However, high temperatures lead to a loss of mechanical strength. A question arises from these previous observations: is there any equivalence between a treatment of short time carried out at high temperature and a treatment of longer time at lower temperature? Answering this question can help to optimise retification temperature and duration. The purpose of this study is to evaluate the relevance of a “time temperature equivalence” (TTE) for wood pyrolysis in the temperature range of retification. The principle of TTE is adapted from the study of wood viscoelastic properties. In this study, it is applied to the rate of anhydrous weight loss during wood pyrolysis. Thermo-gravimetric analysis (TGA) were performed on maritime pine (*Pinus pinaster Ait.-*) and beech (*Fagus sylvatica*) wood powder. Isothermal degradations were carried out at different temperatures ranging from 160°C to 260°C. A specific data analyse was carried out on the TGA derivative (DTG) in order to assess the relevance of the TTE in the temperature range of retification. It gave interpretable results for maritime pine, but not for beech. It showed that for maritime pine wood the TTE is confirmed from 200°C to 220°C, and not confirmed for temperatures superior to 230°C. An optimization of the temperature and time of treatment is thus possible.

## INTRODUCTION AND THEORETICAL CONSIDERATIONS

### *Short presentation of retification treatment*

Retification (Armines 1986) is a heat treatment which consists in a mild pyrolysis of wood (180°C-260°C). It takes place in a non oxidative atmosphere (nitrogen). This treatment decreases the swelling of wood (Repellin and Guyonnet 2005) and increases its resistance to fungal attack (Kamdem *et al.* 2002, Mouras *et al.* 2002) without the use of chemicals. However, the main drawback of wood heat treatment is an important decrease of mechanical strength (Repellin and Guyonnet 2003).

As a consequence, the commercial and industrial development of the retified wood would be made easier if it were possible to minimize the loss of mechanical strength. The purpose of this study is to investigate the possibility to optimize heat treatment parameters (duration and temperature) in order to minimize the loss of mechanical strength.

### *Wood pyrolysis*

Wood pyrolysis follows two pathway : slow and fast pyrolysis, which involve many different reactions and products (Shafizadeh 1984, Faix *et al.* 1991).

For temperatures ranging between 200 and 280°C both slow and fast pyrolysis are present, but slow pyrolysis predominates. The main products of wood decomposition by slow pyrolysis are water, carbon dioxide, carbon monoxide, formic acid, acetic acid and furfural.

At temperature superior to 300°C, fast pyrolysis is predominant. Wood constituents decompose rapidly in tar and volatiles of low molecular weight such as methane, formaldehyde, methanol, phenol *etc.* These decompositions are exothermic reactions.

**Table 1: Relationship between low temperature pyrolysis gaseous products and chemical modifications**

| <b>Product of degradation</b> | <b>Chemical reaction<sup>a</sup></b>  | <b>Chemical reaction<sup>b</sup></b>                             |
|-------------------------------|---|--|
| water                         | Hemicelluloses degradation  | Drying and dehydration   |
| carbon dioxide                | Decarboxylation of uronic acids of hemicelluloses and pectins   | Hemicellulose and lignin decarboxylation                         |
| methanol                      | Decomposition of 4-O-methyl groups of uronic acids<br>Decomposition of lignin's syringyl and guaiacyl units | Degradation of hydroxymethyl groups of lignin and hemicelluloses |
| acetic acid                   | hydrolysis of O-acetyl groups of xylan chains.  | Degradation of acetyl groups of hemicelluloses                   |
| formic acid                   | No explanation  | No explanation   |
| furfural                      | No explanation  | Pentosans degradation  |

<sup>a</sup> According to DeGroot *et. al.*, <sup>b</sup> According to Weiland *et al.*

Retification occurs between 180°C and 260°C. Consequently, the gaseous products evolved during rétification are mainly those of slow pyrolysis. Degroot *et al.* (Degroot

*et al.* 1988) studied isothermal decomposition of poplar sapwood (*Populus trichocarpa*) at 250°C. Weiland *et al.* (Weiland *et al.* 1998) studied the chemical modification of wood powder of chestnut tree (*Castanea sativa*), Norway pine (*Pinus sylvestris*) and maritime pine (*Pinus pinaster* Ait.-) from room temperature to 350°C. The relationship between the evolved gases and the corresponding degradation mechanism are presented in table 1, as proposed by these two authors.

It can be seen (Table 1) that the evolved gases come mainly from hemicelluloses and lignin degradation. Nevertheless, cellulose degradation is not excluded. It is known that gases released during cellulose degradation by pyrolysis are water, carbon monoxide, and carbon dioxide, and (Browne 1958), and these three gases (Weiland *et al.* 1998) are indeed released during retification. Thus the degradation of the three constituents of wood (hemicelluloses, lignin and cellulose) may occurs during heat treatment of wood.

Cellulose is often considered as responsible for the mechanical strength of wood. Consequently, as soon as cellulose begins to decompose, loss of mechanical strength may take place. Nevertheless, hemicelluloses may also play an important part in wood strength. Some authors found a correlation between the decrease of mechanical strength and the degradation of hemicelluloses by brow-rot fungi (Winandy 1993).

### ***Hypothesis concerning pyrolysis reactions***

It is postulated here that the reactions involved in wood pyrolysis may be classified into two groups. Both group induce an increase of stabilization and durability and a decrease of mechanical strength. However, the First group favours stabilization and durability whereas the second favours mechanical strength loss (Table 2). In the range of retification temperature a competition between these two groups is likely to happen.

***Table 2: The postulated two groups of wood pyrolysis reactions.***

| <b>Properties modification</b>  | <b>First group</b> | <b>Second group</b> |
|---------------------------------|--------------------|---------------------|
| Increase of stability           | ++                 | +                   |
| Increase of durability          | ++                 | +                   |
| Decrease of mechanical strength | +                  | ++                  |

At low temperature (200°C) only slow pyrolysis reaction (first group) may be taken into account. Other reactions can be neglected.

When the treatment temperature increases, fast pyrolysis reaction and cellulose destruction (second group) are enhanced.

According to these hypothesis, it would be profitable to carry out the heat treatment at low temperature. In the same time, the improvement of wood end use properties depends on the strength of the treatment. The material modification (that match to the anhydrous weight loss) must be high enough to provide good biological resistance and stabilization to the wood. Thus, a decrease in temperature of treatment should be associated with an increase in the treatment duration, since anhydrous weight loss increases with increasing temperature and duration.

Both reactions of the first and second group obviously result in anhydrous weight loss. By another way, anhydrous weight loss is the only mean to control the advancement and the rate of wood pyrolysis. The rate of anhydrous weight loss should depend on the type of reaction involved. In particular, reactions of the first groups and reactions of the second group should result in different values of the rate of anhydrous weight loss.

On these grounds, if the contribution of each group of reaction is the same over the range of temperature (180°C to 260°C), then, there should be an equivalence between a treatment of short time carried out at high temperature and a treatment of longer time at lower temperature as regards the rate of anhydrous weight loss.

The purpose of this study is thus to evaluate the relevance of a “time temperature equivalence” (TTE) for wood pyrolysis in the temperature range of réтификаtion.

### ***Principle of time temperature equivalence (TTE)***

The principle of TTE is adapted from the study of wood viscoelastic properties (Pluvinage 1992). It may be expressed as follow. The value of a measurable quantity is the same at high temperature for short time as at low temperature for long time.

The TTE principle is observable for instance, when measuring the dynamic flexural vibration of wood beams. For a given range of frequency, the real part of the complex modulus of elasticity has the same value whether it is measured at high temperature for short time of exposure, or at low temperature for a long time of exposure.

Consider a quantity R, that can be measured on a wood sample at two different temperatures ( $T_{ref}$  and T) that belong to a given range of temperature. The TTE is verified if: for any value of R, the time t (that takes to reach R at temperature T) and the time  $t_{Tref}$  (that takes to reach R at temperature  $T_{ref}$ ) are linked by Eqn. 1:

$$t_T = \frac{t_{Tref}}{\alpha_T} \quad (1)$$

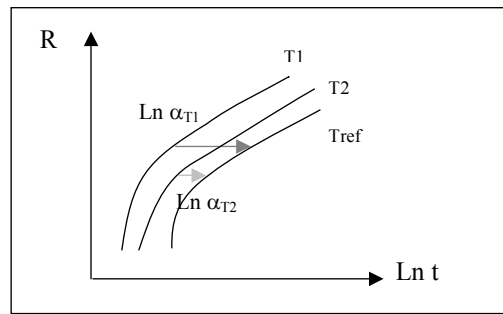
where  $\alpha_T$  is called the translation factor. It depends only on the temperature and it is constant versus time. The TTE principle can also be written (Eqn. 2):

$$R=R(t_{Tref}, T_{ref})=R(t_T, T)=R(t_{Tref}/\alpha_T, T) \quad (2)$$

And Eqn. 1 leads to :

$$\ln(t_T)=\ln(t_{Tref})-\ln(\alpha_T) \quad (3)$$

According to Eqn. 2 and Eqn. 3, when R is plot against  $\ln(t)$ , isothermal curves have to superpose by a translation of  $\ln(\alpha_T)$  (Figure 1).



**Figure 1: Principle of time temperature equivalence**

Thus, an equivalence between the effect of treatment duration and the effect of treatment temperature can be found when any isothermal curve superposes on the isothermal curve obtained at  $T_{ref}$ , by horizontal translation (Figure 1).

In order to check if the TTE principle is confirmed in the temperature range of retification, thermo-gravimetric analysis (TGA) were carried out. Isothermal DTG (TGA derivative) curves were plot and analysed, in order to assess the relevance of the TTE in the temperature range of réтификаtion with regard to the rate of anhydrous weight loss. In this study, R is a given value of the DTG.

### ***The purpose of this study***

This study aims to test the TTE with regard to the rate of anhydrous weight loss, in the range of temperature of réтификаtion (180-260°C).

If this TTE principle is confirmed over a given range of temperature, the modification of the material will be the same at any temperature in this particular range for a given anhydrous weight loss. In this temperature range, it will be possible to increase the temperature and reduce the duration without further degradation of wood constituents due to the second group of reactions.

On the contrary, if the temperature exceeds the temperature range where the TTE is verified, the second group of reactions will induce further degradation of some of the material constituents and increase the loss of strength of the material.

## **EXPERIMENTAL**

### ***Samples***

Natural wood powder was obtained by grinding and sieving specimens between 150 and 212  $\mu\text{m}$ . The samples were made of 10 mg of wood powder. Two species were studied : maritime pine (*Pinus pinaster Ait.-*) and beech (*Fagus sylvatica*). Before experiment, these samples were stored at room temperature and hygrometry.

### ***Method***

The device was a thermobalance NETSCH TG 209. The temperature program was set as follow:

- a ramp from 30°C to 150°C at 30°C/min,
- an isotherm at 150°C during 20 min, in order to dry the sample until its anhydrous state,
- a ramp from 150°C to the chosen temperature (from 160°C to 260°C), at 99°C/min
- an isotherm at the chosen temperature, with a duration ranging from 3 hours to 8 hours depending on the temperature (Table 3).

The reproducibility was evaluated and each isothermal ATG curve was carried out three times.

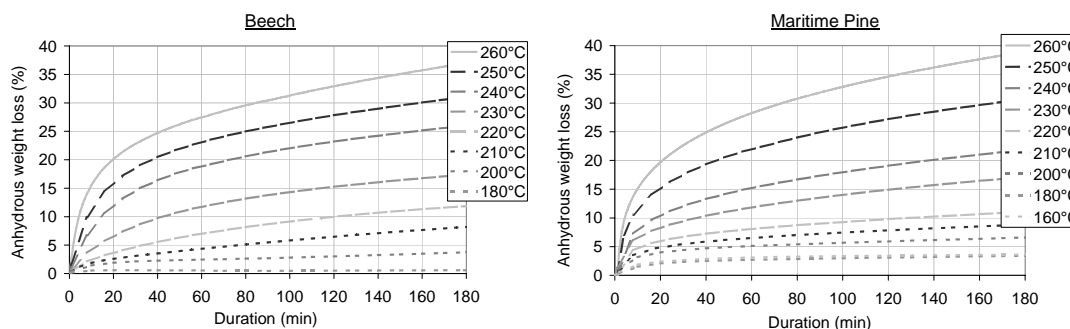
*Table 3: Duration of isotherm at different temperatures*

| Temperature (°C) | Isotherm Duration (hours) |       |
|------------------|---------------------------|-------|
|                  | Maritime Pine             | Beech |
| 160              | 24                        | -     |
| 180              | 24                        | 40    |
| 200              | 16                        | 12    |
| 210              | 9                         | 10    |
| 220              | 5                         | 5     |
| 230              | 5                         | 5     |
| 240              | 3                         | 3     |
| 250              | 3                         | 3     |
| 260              | 3                         | 3     |

## RESULTS AND DISCUSSION

### *Presentation of ATG curves and choice of a reference temperature $T_{ref}$*

The ATG isotherm of beech at 180°C presents no weight loss during three hours (Figure 2). At 160°C and 180°C, the maritime pine isotherms present a loss of weight during the first 20 min. Above 20 min, their weight is constant. Moreover, isotherm at 160°C and 180°C are superposed. We suggest that the weight loss at the beginning of the isotherm corresponds to resin evaporation. Since the weight stabilizes, it is also suggested that no degradation of wood constituents occurs at this temperature.

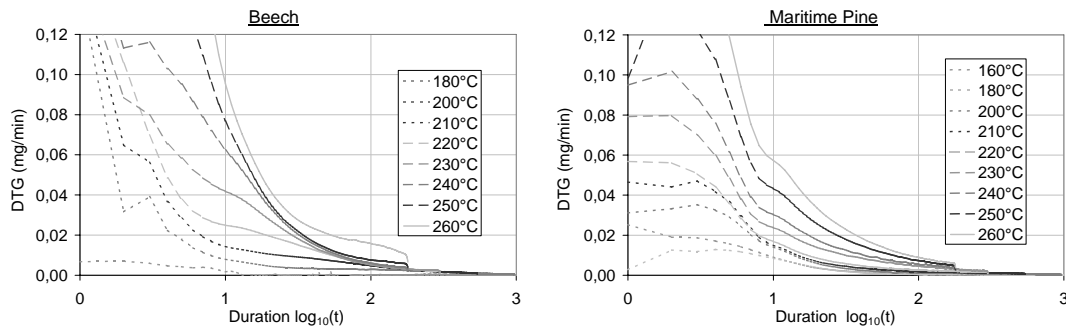


*Figure 2: TGA of Beech and Maritime Pine wood.*

At 200°C both beech wood and pine wood loose weight. This loss of weight increases when the duration increases, and should thus be due to wood degradation by pyrolysis reactions. Since 200°C is the lowest temperature at which degradations seem to happen, we chose it as the reference temperature ( $T_{ref}$ ).

### ***TTE during the first 30 minutes***

The DTG curves are presented versus the decimal logarithm of time (Figure 3), in order to check the TTE principle.



**Figure 3: DTG of beech and maritime pine wood**

On these two graphs (Figure 3), the TTE principle is verified when the DTG curves can be superposed on each other by an horizontal translation. The first 3 first minutes are instable are not discussed.

For maritime pine, it is obvious that TTE is not verified all over the temperature range studied. For a given rate of weight loss, the slope of the DTG curves varies with increasing temperature. This is well visible on maritime pine DTG curves, and less visible for beech wood.

The beech seem to be less resistant and stable than maritime pine at the beginning of the isotherm. Its rate of weight loss is higher than the rate of weight loss of maritime pine, and beech wood DTGs seem to be scattered in the first minutes of isotherm. Consequently, it is not easy to assess if the TTE principle is confirmed or not for beech.

Nevertheless, for beech and maritime pine, superposition of isotherms at 210 and 220°C on the isotherm at 200°C by horizontal translation seem to be possible. During the first half hour, for maritime pine as well as for beech, the TTE seem to be verified from 200°C to 220°C, and not verified for temperatures superior or equal to 230°C.

### ***TTE for durations superior to 30 minutes***

It is not possible to see on figure 3 if the TTE is confirmed after 30 minutes (Figure 3). That is why, we calculated  $t/t_{Tref}$  (Eqn. 1). According to Eqn. 2 and Eqn. 3, when the TTE is verified  $\ln(\alpha_T)$  (and consequently  $t/t_{Tref}$ ) is constant versus R, and should depend only on the temperature.



Figure 4 shows  $t/t_{Tref}$  at different values of R and of the temperature of isotherm. when it is constant versus R, it can be concluded that the TTE principle is confirmed. When it is not constant, the TTE principle is not valid.

Concerning beech wood, it is impossible to give any conclusion concerning the TTE principle. The values of  $1/\alpha_T$ , are too scattered to see if it is constant in function of R. We suggest that it is a consequence of hardwood thermal instability, which is known to be higher than thermal instability of softwood.

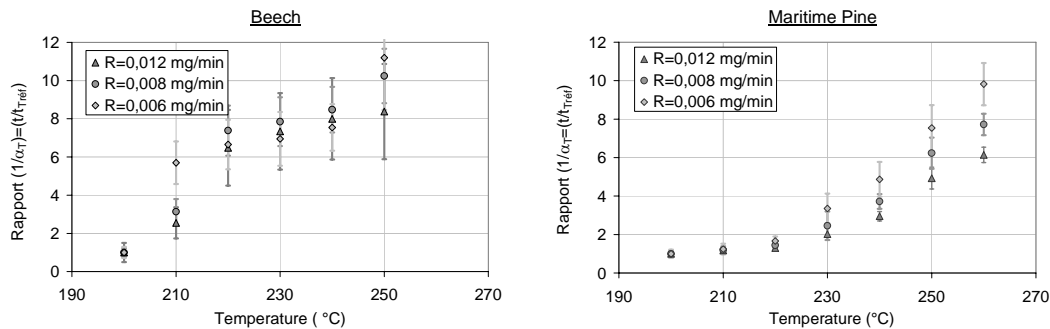


Figure 4:  $1/\alpha_T$  in function of temperature, for different values of R.

Concerning maritime Pine,  $t/t_{Tref}$  is almost constant versus R at 210°C and 220°C. It increases with R at any temperature superior or equal to 230°C. This increase is enhanced with temperature augmentation. This observation suggests that for maritime pine, TTE is almost confirmed between 200 and 220°C, and is not verified at temperatures superior to 230°C. Moreover, as the difference of temperature with reference temperature increases, the TTE principle becomes more and more wrong.

## CONCLUSIONS

Time and duration of heat treatment are crucial parameters to obtain a material with good properties. In this study a methodology (the TTE principle) is adapted from the study of wood viscoelastic properties. It is applied to beech and maritime pine wood powder in order to assess the possibility to optimise treatment time and duration.

Isothermal DTG were analysed according to this TTE principle. It gave relevant results for maritime pine, but not for beech wood. We suggest that it is a consequence of the lower thermal stability of hardwood than thermal stability of softwood.

For temperatures ranging between 200°C and 220°C, the TTE principle seem to be confirmed for maritime pine. The temperature can be thus increased until 220°C without further loss of mechanical strength. This is not the case for temperatures superior to 230°C, at which reactions that favour mechanical strength loss should be enhanced.

An optimisation of heat treatment parameters is thus possible for maritime pine wood. At first, temperature of treatment should not exceed 220°C. Secondly, in the range of temperature from 200°C to 220°C, the duration has to be increased until the material reaches a certain anhydrous weight loss.

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