Thermal modification of birch wood to obtain desired color

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Abstract. Thermomodification is a thermal destruction of wood in an oxygen-free environment. The actual problem is the analytical identification of technological regimes for obtaining thermomodification wood with desired properties, including color parameters. The rate of thermal destruction depends on the temperature, kinetic parameters of each stage and the degree of completion. The article proposes to determine the wood color characteristics as a function of degree completion individual stages of thermal destruction. To identify used model of color components decomposition at the GRB. A method for determining the degree of wood modification by its color is proposed. The mathematical model for calculation of technological process parameters thermomodification to get wood of set color is resulted. An example of determining the degree of thermal destruction industrial production birch wood by color parameters is given. Technological modes for production of set color wood are calculated. Solutions are obtained for isothermal and non-isothermal regimes.

1. Introduction

Wood is a unique, widespread in nature material. It is used as structural and finishing materials. Wood has a number of significant advantages over other materials – environmental cleanliness, relative ease of processing, neutrality with respect to the person, the constant renewal of sources, etc. On the other hand, the wood has disadvantages – the possibility of biological lesions, instability of geometric dimensions and shape when changing humidity, relative fragility.

For improvement of consumer and operational properties of wood heat treatment is widely applied. These processes include drying and various types of modification, including thermal modification of wood.

Thermal modification is a process of thermal degradation in an oxygen-free environment. When heated, the destruction of wood components – hemicelluloses, cellulose, lignin. These components have different chemical bonds, the intensive destruction of which occurs in different temperature ranges, and these ranges can partially overlap [1-6]. Thermal decomposition of hemicelluloses, cellulose and lignin occurs at 225-325 °C, 305-375 °C and 250-500 °C, respectively [7]. This leads to the multistage process of thermal degradation. Complex physical and chemical processes occurring in the wood during thermal destruction can be described using the Arrhenius equation:

$$\frac{d\omega}{d\tau} = \omega A \exp\left(\frac{-E}{RT}\right),$$

(1)
where, $A$ – frequency factor, ($s^{-1}$); $E$ – activation energy, (J/mol); $R$ – universal gas constant, (J/mol·K); $T$ – temperature, (K); $\omega$ - dimensionless mass.

Often the process is considered as a one-stage, but the kinetic parameters obtained in this case depend on the heating rate, which limits their applicability. The actual processes of thermal degradation of wood are multi-stage. They can be considered as parallel, independent chemical reactions. The speed of a multistage process can be described by the equation:

$$\frac{d\omega_j}{d\tau} = \sum_{j=1}^{n} \omega_j A_j \exp\left(-\frac{E_j}{RT}\right),$$

(2)

where, $j$ is the stage number; $n$ is the number of stages.

To determine the kinetic parameters of thermal destruction stages it is necessary to conduct thermogravimetric researches.

To determine the post-stage kinetic parameters of thermal destruction, we use the method proposed by B A Shvedov [8].

Experimental and computational researches of birch wood thermal destruction kinetics were carried out [9]. Thermogravimetric experiments were carried out in a environment of inert helium gas. The results of the thermogravimetric experiment are shown in Figure 1. Figure 2 shows a graph of the rate change relative mass of the sample.

After processing the results of experimental researches, the kinetic parameters of the thermal degradation stages were calculated. The calculation results are shown in Table 1.

Based on certain kinetic parameters, the change relative mass and the rate of change relative mass of sample in the thermogravimetric experiment were calculated. The calculated values are shown in Figure 1 and Figure 2 dots.

Thermal modification leads to changes in the composition and structure of the wood, which causes a change in properties. The properties of the resulting material depend on the degree of thermal degradation.

![Figure 1. Change relative mass of sample.](image1)

![Figure 2. Rate of change relative mass of sample.](image2)
It is convenient to use the RGB color decomposition model to identify a color. Experimental studies have been conducted on the dependence of the color of thermally modified wood on the degree of thermal degradation [10]. The studies were carried out using the method of unsaturated decomposition of samples. When preparing the samples, the thermal modification modes are selected in such a way that the stages of the thermal destruction process, starting with the first, are successively completed. During the heat treatment of samples in helium, the surface temperature was recorded, and then the degrees of completion of all stages of the thermal destruction process were calculated.

The samples prepared in this way were used to study the dependence of material color on thermal destruction degree. The relative masses of the sample stages and their color characteristics are shown in Table 2.

### Table 1. Kinetic parameters of thermal degradation birch wood in helium.

| Breed of wood | Stage number | Stage speed maximum temperature, $T_{\text{max}}$, K | The temperature of the stage beginning, $T_{\text{start}}$, K | The temperature of the stage end, $T_{\text{end}}$, K | Initial stage weight, $\omega_0$ | Activation energy, $E/R$, K | Frequency factor, $A$, c^{-1} |
|---------------|--------------|--------------------------------|--------------------------------|--------------------------------|------------------|-----------------|-----------------|
| Birch         | 1            | 552                           | 502                          | 584                          | 0.026            | 2.569$\times10^8$ | 12530           |
|               | 2            | 598                           | 547                          | 622                          | 0.119            | 6.637$\times10^{17}$ | 25006           |
|               | 3            | 605                           | 534                          | 639                          | 0.571            | 1.227$\times10^{11}$ | 18310           |
|               | 4            | 661                           | 459                          | 791                          | 0.134            | 314.000         | 8069            |
|               | 5            | 800                           | 611                          | -                            | 0.151            | 1.383$\times10^4$   | 12850           |

### Table 2. The study results of wood RGB color parameters by method of unsaturated decomposition

| Sample number | Relative weight of sample after heat treatment | Relative mass of the thermal decomposition stage | Results of processing digital photos in Photoshop editor |
|---------------|-----------------------------------------------|-----------------------------------------------|------------------------------------------------------|
|               | $\omega_1$ | $\omega_2$ | $\omega_3$ | $\omega_4$ | $\omega_5$ | $R$ | $G$ | $B$ |
| 1             | 1.000       | 0.026       | 0.119     | 0.571     | 0.134    | 0.151 | 226 | 217 | 205 |
| 2             | 0.999       | 0.024       | 0.119     | 0.571     | 0.134    | 0.151 | 160 | 133 | 100 |
| 3             | 0.998       | 0.023       | 0.119     | 0.571     | 0.134    | 0.151 | 157 | 126 | 89  |
| 4             | 0.993       | 0.019       | 0.119     | 0.571     | 0.133    | 0.151 | 143 | 108 | 72  |
| 5             | 0.961       | 0.000       | 0.110     | 0.568     | 0.132    | 0.151 | 121 | 90  | 61  |
| 6             | 0.906       | 0.000       | 0.070     | 0.555     | 0.130    | 0.151 | 57  | 48  | 45  |

Substituting obtained values RGB parameters of the experimental values in the expression (3), we obtain a system of equations. Solving the obtained system, we determine the coefficients for approximation of parameter $R$. Similarly, the approximation coefficients for parameters $G$ and $B$ can be defined. As a result, equations describing the dependence of the parameters $R$, $G$ and $B$ on relative masses first three stages of birch wood thermal destruction were obtained:

$$R(\omega) = 226 - 3692(\omega_{0,1} - \omega_1) - 1018(\omega_{0,2} - \omega_2) + 1018(\omega_{0,3} - \omega_3)^2 - 24(\omega_{0,3} - \omega_3). \quad (3)$$

$$G(\omega) = 217 - 4366(\omega_{0,1} - \omega_1) - 1572(\omega_{0,2} - \omega_2) + 9137(\omega_{0,3} - \omega_3)^2 - 24(\omega_{0,3} - \omega_3), \quad (4)$$

$$B(\omega) = 205 - 5597(\omega_{0,1} - \omega_1) - 394(\omega_{0,2} - \omega_2) + 2240(\omega_{0,3} - \omega_3)^2 - 33.8(\omega_{0,3} - \omega_3). \quad (5)$$


Equations (3–5) allow to calculate RGB color parameters of birch wood after thermal modification. The relative masses of stages $\omega_i$ included in the equations are determined from the solution of the direct kinetic problem:

$$T = T(\tau, x),$$

$$\omega_i(T, \tau) = \omega_{0i} \exp\left[-A \int_{\tau_i}^{\tau} \exp\left(-\frac{E_i}{RT}\right) d\tau\right]$$

(6)

(7)

3. Results and Discussion

To solve the problem optimization of technological parameters to obtain a given color, it is necessary to determine the RGB parameters corresponding to the real color of thermally modified wood. Consider the problem determining the birch wood thermal modification modes to obtain a color corresponding to the color of the existing sample. As an example, take the wood that is modified in the flue gas according to the following regime:

- The first stage is heating. The coolant temperature varied at a steady rate $\Delta T=7$ K/h to $T_{\text{max}} = 175$ °C;
- The second stage – exposure at a constant temperature $T_{\text{max}} = \text{const}$;
- The third stage is cooling.

RGB color components of the sample ($R_e=125$, $G_e=89$, $B_e=57$) were determined. Using the obtained values of the color parameters it is possible to determine the values of the current relative masses $\omega_1, \omega_2, \omega_3$ stages of thermal destruction. These values can be determined from the solution of the system of equations (3) – (5). To solve the system, we use optimization methods, the method of coordinate-wise descent. As a target function, we use the standard deviation calculated RGB values of the parameters from the experimental ones:

$$S = \left\{ \left[ R_e - R(\omega_1, \omega_2, \omega_3) \right]^2 + \left[ G_e - G(\omega_1, \omega_2, \omega_3) \right]^2 + \left[ B_e - B(\omega_1, \omega_2, \omega_3) \right]^2 \right\}^{\frac{1}{2}},$$

(8)

where, $R_e, G_e, B_e$ are the color parameters of the original sample; $R(\omega_1, \omega_2, \omega_3), G(\omega_1, \omega_2, \omega_3), B(\omega_1, \omega_2, \omega_3)$ – color options is designed according to the relations (3) – (5). We solve the problem of determining the minimum of the objective function:

$$S(\omega) \rightarrow \min_{\omega \in \Omega},$$

(9)

where, $\omega = (\omega_1, \omega_2, \omega_3)$.

After solving the problem, we obtain current values relative masses of the thermal destruction stages corresponding to the given color:

$$\omega = (0.0002, 0.1102, 0.5710)$$

(10)

Based on this information and source material properties, the material thermal properties – density, heat capacity and thermal conductivity coefficient can be determined.

Having information about current values of thermal degradation stages relative masses, it is possible to calculate the modes of technological processes for obtaining a material with specified properties, including a given color.

Thermal modification of wood technologies include following main stages – heating at a constant rate to a given temperature, aging at a given temperature and cooling. The cooling stage has almost no
effect on the change in the properties of wood. The main changes occur at the stage of exposure at maximum temperature. They are determined by multi-stage physical and chemical processes occurring in the wood and depend on the completion degree of the individual stages. The current values of stages relative masses are described by equation (7). This equation includes two parameters that determine the mode of the process – temperature and time of exposure. Thus, to solve the problem you need to set additional restrictions.

As restrictions can be set exposure time $\tau_{\text{set}}$:

$$\tau_{p} = \tau_{\text{set}} = \text{const}$$  \hspace{1cm} (11)

Solving equation (7) with respect to $T$ we obtain:

$$T = -E_i \ln \left( \frac{\omega_{b,i}}{\omega_i(T, \tau)} \right) \left( \frac{RT}{A_i \cdot \tau} \right)^{-1}$$  \hspace{1cm} (12)

where $i$ is the stage number.

The calculation is advantageously carried out for stage, which has begun but not fully completed. In this example, this is the second stage.

The exposure temperature can also be set as a limit:

$$T = T_{\text{set}} = \text{const}.$$  \hspace{1cm} (13)

Solving equation (7) with respect to $\tau_{p}$ we obtain:

$$\tau_{p} = \frac{\ln \left( \frac{\omega_{b,i}}{\omega_i(T, \tau)} \right) \exp \left( \frac{E_i}{RT} \right)}{A_i},$$  \hspace{1cm} (14)

Recommendations for choosing the stage remain the same.

The results of the isothermal effect regimes calculations are given in Table 3. All modes given in the table allow get wood of the set color.

Real technological impacts are not isothermal. Let us consider a two-stage process, including a stage of temperature increase at a constant rate and a stage of isothermal action at maximum temperature. The cooling stage is excluded from consideration, since it practically does not affect the color change.

**Table 3.** Wood modification parameters to obtain a given color.

| Reference variable | Design parameter | The relative weight of the phases after heat treatment | RGB settings for the wood color after heat treatment |
|--------------------|------------------|-----------------------------------------------------|---------------------------------------------------|
| $T=175 \, ^\circ C$ | $\tau=56 \, h$   | $\omega_1$ | $R$ | $G$ | $B$ |
| $T=180 \, ^\circ C$ | $\tau=30 \, h$   | $\omega_2$ | $0.110$ | $0.571$ | $122$ | $91$ | $57$ |
| $T=185 \, ^\circ C$ | $\tau=16.5 \, h$ | $\omega_3$ | $0.000$ |          |              |              |
| $T=170 \, ^\circ C$ | $T=160 \, ^\circ C$ |              |              |              |              |
| $T=100 \, ^\circ C$ | $T=173 \, ^\circ C$ |              |              |              |              |
| $T=70 \, ^\circ C$ | $T=189 \, ^\circ C$ |              |              |              |              |
To obtain the corresponding calculated relations, replace the integral in equation (7) with a numerical approximation using the trapezoid method:

\[
\omega_j(T, \tau) = \omega_{0,i} \exp \left[-A_i \left( \exp \left( \frac{-E_i}{RT_0} \right) + \exp \left( \frac{-E_i}{RT_{max}} \right) \tau_1 + \exp \left( \frac{-E_i}{RT_{max}} \right) (\tau - \tau_1) \right) \right],
\]

(15)

where, \( \tau_1 \) is the warm-up stage time, s; \( \tau \) is the total time of the warm-up and holding stages, s.

Solving equation (15) with respect to \( \tau \) and \( T_{max} \) we obtain correspondingly:

\[
\tau = - \frac{2 \ln \left( \frac{\omega_j(T, \tau)}{\omega_{0,i}} \right) \exp \left( \frac{E_i}{RT_{max}} \right) - A \tau_1}{2A_i}
\]

(16)

\[
T_{max} = -E_i \left[ R \ln \left( \frac{2 \ln \left( \frac{\omega_j(T, \tau)}{\omega_{0,i}} \right) + A \tau_1 \exp \left( \frac{-E_i}{RT_0} \right)}{A \tau_1 - 2A \tau} \right) \right]^{-1}
\]

(17)

where, \( T_0 \) is the initial temperature of the material, K;

\[
\tau_1 = \frac{T_{max} - T_0}{\Delta T}.
\]

(18)

The results of calculations of the two-stage exposure modes are given in Table 4.

**Table 4. Calculation results of two-stage modes.**

| Reference variable | Warm-up time, h | Holding time, h | Defined parameter |
|--------------------|----------------|----------------|------------------|
| \( T_{max} = 175 \, ^\circ C \) | 22.1           | 46.3           | \( \tau = 68.4 \, h \) |
| \( T_{max} = 180 \, ^\circ C \) | 22.9           | 19.5           | \( \tau = 42.4 \, h \) |
| \( T_{max} = 185 \, ^\circ C \) | 23.6           | 5.1            | \( \tau = 28.7 \, h \) |
| \( \tau = 30 \, h \) | 23.5           | 6.0            | \( T_{max} = 184.6 \, ^\circ C \) |
| \( \tau = 50 \, h \) | 22.6           | 27.0           | \( T_{max} = 178.0 \, ^\circ C \) |
| \( \tau = 70 \, h \) | 22.1           | 47.7           | \( T_{max} = 174.8 \, ^\circ C \) |

Analyzing the data given in Table 4, it can be concluded that the calculated process parameters are well correlated with the temperature and heating time of the sample.

**4. Summary**

The choice of a particular regime may be based on additional conditions or restrictions. Among them may be the technical capabilities of process unit, the minimum energy consumption, the minimum cycle time, etc. Comparison of results given in table 3 with the actual mode thermal modification of the original sample shows their satisfactory agreement. Thus, at a given temperature of exposure \( T = 175 \, ^\circ C \), the estimated process time is \( T_p = 56 \, h \). This agrees satisfactorily with the real regime (time step of aging 47.9 hours).
When calculating the two-stage heating at a temperature of impact $T=175$ °C, the estimated process time is $T_p = 68.4$ hours, which satisfactorily coincides with the real mode of thermal modification of the sample.

Thus, the proposed model (3-14) allows calculating the optimal parameters values of wood thermal modification process, allowing obtaining a material with a given color. The model allows determining the degree of wood thermal destruction by its color. It is obvious that this approach allows determining parameters of wood thermomodification to obtain a material with other specified properties.

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