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Fast growing *Paulownia* wood – perspective raw material for production of fibrous materials

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The present paper is intended to make a comparative kinetic analysis of the effect of bleaching pretreatment and temperature increase on the thermal ageing of fiber material derived from fast growth Paulownia wood. The brightness reversion of bleached and unbleached samples is followed within the interval from 6 to 72 hours. The temperature values studied refer to 90^0C, 105^0C and 120^0C. Exponential kinetic equation is applied for description of the ageing process kinetics by means of which the initial and current rates of the process are calculated. The values of the activation energy and the pre-exponential factor in the Arrhenius equation applied increase simultaneously in the course of the process.

Key words: *Paulownia wood, Brightness, Thermal aging, Kinetic analysis*

1. INTRODUCTION

The low-cost raw forest products and the processes providing the use of wood biomass could solve the problem with the scarce natural resources. Paulownia is a deciduous tree capable of achieving very height growth rates under favorable conditions. Under good growth conditions these trees will reach 15 m in height and will produce commercially harvestable timber in 7-10 years. This deciduous tree has been widely used for construction, pulping, furniture making and handicrafts [1, 2].

Semi chemical pulping process is a two-stage method. It combines chemical treatment aimed at lignin partial removal and a mechanical refining step leading to defibring [3-5]. The semi chemical pulps produced on the ground of hardwoods have higher strength but relatively low brightness when compared to that obtained from softwoods. Because of the lignin content the unbleached samples of semi chemical pulps (CMP) age faster than the bleached one. The yellowing starts with the oxidation of the lignin phenolic hydroxyl groups, which in turn leads to the subsequent formation of quinones, quinone-methydes and cyclohexadienes [6-8].

Ageing is a complicated process, because the rate of changes in the fiber materials depends on the temperature, on the amount of the bleaching reagents, on the degree of the delignification, on the mass concentration, on the bleaching sequence, on the process duration, as well as on other factors [9].

The study of the kinetics of semi chemical pulp thermal ageing is expected to provide data whose treatment may facilitate to elucidate its mechanism and hence to optimize the process accounting as well the advantages of the methods of treatment and storage. The problem is that ageing is a complex process which does not obey formal kinetic principles.

The purpose of this study is to investigate and analyze the kinetics of the artificial thermal ageing of bleached and unbleached chemical mechanical pulps obtained from *Paulownia tomentosa*.

2. EXPERIMENTAL

The experiments were carried out with a pulp obtained from *Paulownia tomentosa*. Chemical mechanical pulp (CMP) was obtained under the following conditions: 100 g absolutely dry strips, hydromodule of 1:5, treatment temperature of 80^0C, duration of 120 min, with addition of 8% NaOH and 5% Na_2SO_3. The oxidation reagent: H_2O_2 was added in concentration of 2%. The concentrations are evaluated in respect to the mass of the absolutely dry strips used. CMP yield was 86% (determined by the weight method), while the degree of refining was 13^0SR. (the measurements were conducted on a Schopper-Riegler (^{o}SR) equipment in correspondence with the EN ISO 5267 – 1/AC:2004).

CMP prepared under the conditions pointed above was subjected to a two-stage combined bleaching, i.e. bleaching with oxidation reagent: H_2O_2 (I stage) followed by bleaching with the reducing agent Rongalyt C (II stage). The first stage was applied to CMP at 70^0C within 120 min. In this case the pH is 10.5, while the amount of H_2O_2 was

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again 2%. The additives used referred to 2% NaOH, 5% Na_2SiO_3, 0.5% $MgSO_4$ and 0.5% EDTA ($Na_2C_{10}H_{14}O_8N_2.2H_2O$) as a complexing agent. All amounts pointed so far were calculated in respect to the absolutely dry fibrous material used. The procedure applied required to place the sample in a polyethylene bag, to bring it to the temperature value envisaged and then to introduce the bleaching solution under constant stirring aiming complete homogenization. Rongalyt C ($NaHSO_2.CH_2O.2H_2O$) and EDTA were introduced during the second stage of the bleaching process which was carried out for 60min at 70^0C. The consumption of Rongalyt C and EDTA was 1.5% and 0.5%, correspondingly. In this case the pH is 5. The bleaching procedure was analogous to that applied during the first stage. The bleached fibrous material obtained was finally washed until a neutral reaction was obtained.

Samples of unbleached and bleached CMP were subjected to thermal ageing for 72 hours at temperatures of 90^0C, 105^0C and 120^0C. Their brightness and yellowness was determined using "Brightness R_{457} (in correspondence with ISO 2470:2002) prior to and after the ageing. Furthermore, the degree of brightness of the bleached samples was determined at the 6-th, 12-th, 24-th 36-th, 48-th and the 72-th hour of the process.

3. RESULTS AND DISCUSSION

The effect of ageing of CMP is followed on the ground of the comparative investigation of bleached and unbleached samples. The brightness reversion observed in the course of the thermal ageing of the samples of both types is followed at 90^0C, 105^0C and 120^0C. The values obtained are summarized in Table 1.

Table 1. Values of the degree of brightness, *W* (%) of CMP – unbleached and bleached, in the course of the process of ageing (h) at the temperature values studied (T^0C).

Time, h	Brightness, *W*, %					
	T=90^0C		T=105^0C		T=120^0C	
	unbleached	bleached	unbleached	bleached	unbleached	bleached
0	46.31	65.01	46.05	65.60	46.73	65.89
6	44.83	64.47	44.22	63.60	44.26	62.48
12	43.96	62.94	43.57	62.38	43.62	61.57
24	43.85	61.95	43.05	60.79	42.41	60.24
36	42.89	60.85	42.96	60.59	41.75	58.25
48	42.13	59.98	42.76	58.81	41.10	56.74
72	41.98	58.99	42.06	58.03	40.08	56.50

It is seen from Table 1 that the bleached samples have higher degrees of brightness than those of the unbleached one at all temperature values studied. Furthermore, the temperature increase brings about increase of the rate of ageing of the samples of both types. The results presented evidence as well that the brightness of the bleached samples, although higher than that of the unbleached one, shows higher reversion with time and temperature.

The comparative consideration of the characteristics of the thermal ageing kinetics is done with the introduction of the kinetic variable, α:

$$\alpha = \frac{W_0 - W}{W_0} \qquad (1)$$

where W_0 is the initial brightness value in % (ISO), while *W* in % (ISO) is the current value connected with the time of the treatment. The variable α can be also considered as an extent of the thermal ageing proceeding or as a relative decrease of the degree of brightness in the course of the process.

The kinetic curves of the change of α with time (h) obtained for the bleached and unbleached samples at the three temperature values studied are presented in Fig. 1. As Figure 1 shows α increases with time and temperature for both types of samples. This increase of the kinetic variable corresponds to the increase of the extent of the process of thermal ageing, i.e. to the corresponding brightness reversion of CMP.

Various kinetic equations describing the kinetics of processes taking place on homogeneous and heterogeneous surfaces [9-12] have been applied aiming to elucidate the specifics of the ageing process. It was found that the process of ageing is best described by the exponential equation (2) valid for heterogeneous processes taking place on uniformly inhomogeneous surfaces:

$$v = v_0 e^{-a\alpha} \qquad (2)$$

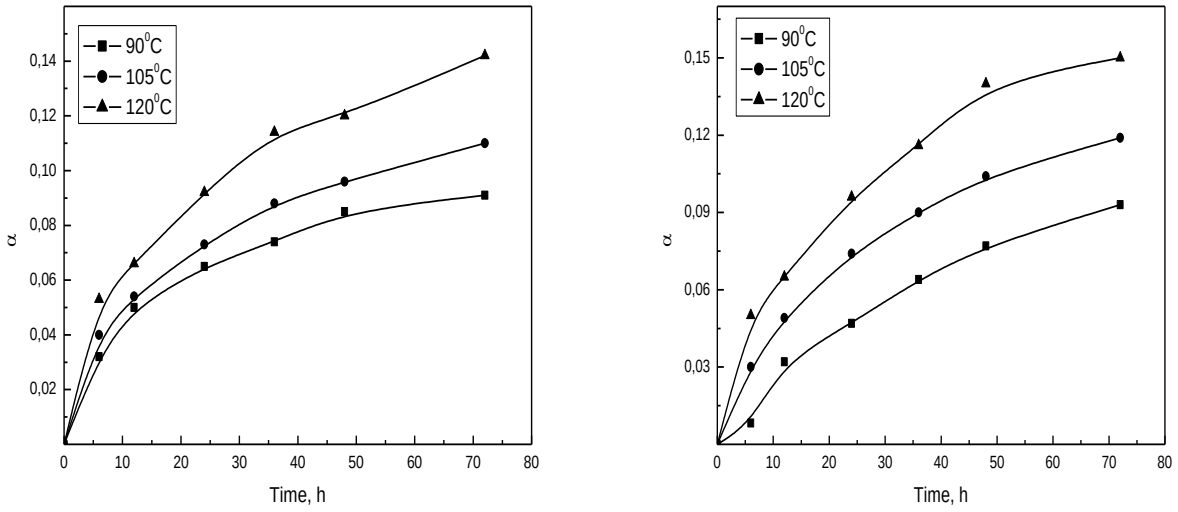
where the current and the initial rate of the ageing process are designated by $v = d\alpha/dt$ and v_0, respectively. In accord with the model of uniformly

inhomogeneous surfaces [10-12] the active centres on the biomass surface are distributed linearly in correspondence with their energy. The kinetic coefficient of inhomogeneity *a* in Equation 2 accounts for the energy and entropy inhomogeneity of the heterogeneous system. All kinetic curves are linearized in coordinates α - ln *t* in correspondence with the approximate integral form of the exponential kinetic equation:

$$\alpha = \frac{1}{a}\ln(v_0 a) + \frac{1}{a}\ln t \qquad (3)$$

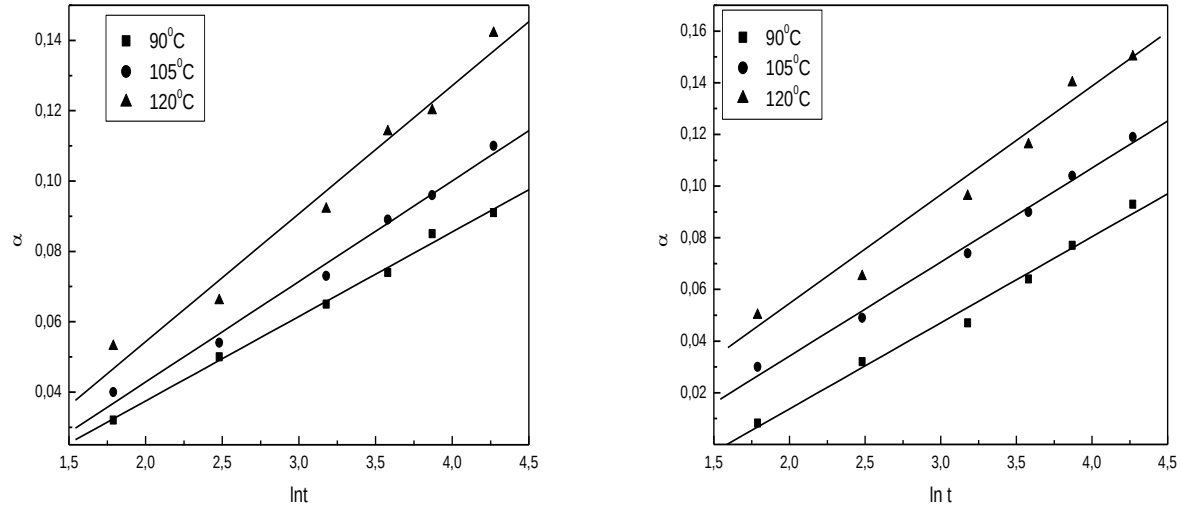
The linear dependences obtained in correspondence with Equation 3 are presented in Figure 2.

The value of the slope of the lines obtained (Figure 2) provides the determination of coefficient of inhomogenety *a* (Equation 3). The values of the latter are presented in Table 3. It is seen that *a* decreases with temperature increase.



(a) (b)

Fig. 1. Kinetic curves of increase of the ageing process extent for: (a) unbleached CMP; (b) bleached CM.



(a) (b)

Fig. 2. Linearization of the kinetic curves in coordinates α-ln *t* for: a) unbleached CMP; b) bleached CMP.

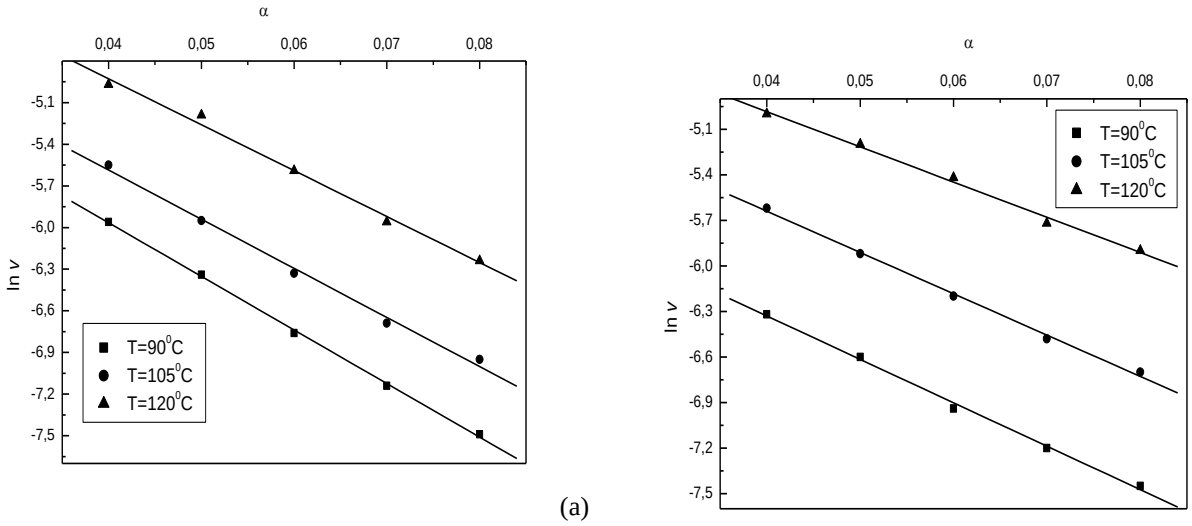
Table 2. Initial and heterogeneity characteristics of the artificial ageing processes.

Temperature	90°C		105°C		120°C	
	unbleached	bleached	unbleached	Bleached	unbleached	bleached
a	41.66	30.03	31.96	27.48	27.47	23.29
$v_0 x 10^3$, h^{-1}	12.03	6.73	15.45	10.84	27.30	24.72

The integral form of the exponential kinetic equation (Equation 3) can be used for the determination of the initial rate, v_0 (h^{-1}), of the process of thermal ageing at $\alpha \to 0$. The values of v_0 are presented in Table 2. The current rate of the process, v (h^{-1}), at different time and temperature values is estimated on the ground of Equation 4 at a constant value of the extent of the process proceeding (α = const):

$$v = \frac{1}{at} \quad (4)$$

The temperature effect is outlined in Figure 3 according to the logarithmic form of Equation 2. The latter shows that the rate of ageing of both samples types decreases with α increase and increases with the temperature increase.



(a) (b)

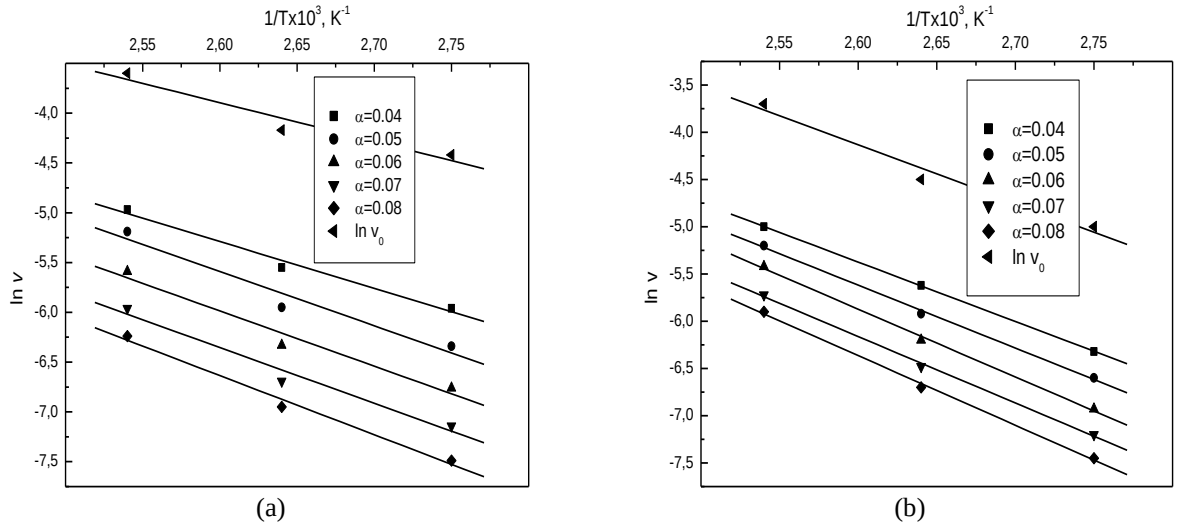
Fig. 3. Dependence of the current rate, ln v (h^{-1}) on α, at the temperature values studied for: a) unbleached CMP; b) bleached CMP.

The temperature effect on the process parameters can be followed through the investigation of the temperature dependence of the initial v_0 and the current rate v on the ground of the Arrhenius equation:

$$\ln v = \ln A - \frac{E}{R}\frac{1}{T} \quad (5)$$

where E (kJ/mol) is the activation energies of the process at different constant values of α, while A is the pre-exponential factors. The values of the activation energy and the pre-exponential factor and their change at different values of α are summarized in Table 3 and Figure 4.

As Figure 4 shows the linear dependences obtained have different slopes, i.e. the values of the activation energy and the pre-exponential factor increase with α increase. That means that the surface is energy and entropy heterogeneous.



(a) (b)

Fig. 4. Temperature dependence of the initial v_0 and the current rate v at α=const in case of: a) unbleached CMP; b) bleached CMP.

The values of the pre-exponental factor and the activation energy increase as well in the course of the process, which indicates that the number of the chromophore groups, responsible for brightness reversion, increases. The total increase of the energy and entropy factors is greater at the bleached samples. Their rate of ageing is lower and

hence it can be concluded that the bleaching hampers in fact the ageing.

Table 3. Values of the activation energy, *E*, kJ/mol and the logarithm of the preexpoential factor, ln *A* at different values of process proceeding, α=const.

α	ln A		E, kJ/mol	
	unbleached	bleached	unbleached	Bleached
0	7.38	8.30	36.10	40.20
0.04	8.77	10.97	43.4	52.27
0.05	9.77	11.69	50.55	55.35
0.06	10.07	12.79	51.38	59.70
0.07	10.20	13.20	51.79	61.30
0.08	11.20	13.71	54.77	64.50

4. CONCLUSIONS

A kinetic analysis of the stability to thermal ageing of samples of bleached and unbleached CMP obtained from *Paulownia tomentosa* is presented. The kinetics of the process is best described by an exponential kinetic equation valid for heterogeneous process. The temperature dependence of the rate is followed and the values of the activation energy and the preexponential factor in the Arrhenius equation are estimated. They are found to increase simultaneously with increase of the extent of the process on the bleached and the unbleached samples.

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БЪРЗОРАСТЯЩАТА ДЪРВЕСИНА ОТ *Paulownia* - ПЕРСПЕКТИВНА СУРОВИНА ЗА ПРОИЗВОДСТВО НА ВЛАКНЕСТИ МАТЕРИАЛИ

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(Резюме)

Целта на настоящата работа е да се направи сравнителен кинетичен анализ на ефекта от избелване и от повишаване на температурата върху термичното стареене на влакнест материал, получен от бързорастяща дървесина от вида Paulownia. Проследено е изменението на оптичните свойства на избелените и неизбелени образци в интервала от 6 до 72 часа. Проследено е стареенето при три температури от 90°C, 105°C и 120°C. За описание на кинетиката на процеса на стареене е приложено експоненциалното кинетично уравнение. Иичислени са началната и текущите скорости на процеса. Установено е, че сстойностите на активиращата енергия и на предекспоненциалния множител, от уравнението на Арениус, нарастват едновременно в хода на процеса.