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Obtaining of high yield fibrous material from hardwood and evalution of their optical properties of in process of thermal treatment

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The main fibrous materials used in the pulp and paper industry are: cellulose, semi chemical pulp, high yield fibrous materials (HYFM) and second fibers. All of them are of plant origin. They are obtained mainly from wood and annual plants.

In this study was used poplar wood species with improved density of type - *Populus deltoids cultivar Hunnegem* with density of 504 kg/m^3. In this research were obtained two types of chemical mechanical pulps (CMP). CMP of Type 1 was obtained with 7% NaOH and 5% Na_2SO_3, and CMP of Type 2 was obtained with 7% NaOH, 5% Na_2SO_3 and 2% H_2O_2. The CMP of Type 1 and 2 were received under the same conditions of temperature, hydromodul ratio, duration of process etc.

Both of Chemical Mechanical Pulps have a low degree of brightness, and therefore they are bleached in two stages. The initial process of bleaching was conducted with H_2O_2 and second stage was performed with Rongalyt C. The samples of both CMP pulps were exposed to artificially thermal ageing at 105°C. The changes of brightness and yellowness in process of the thermal ageing of 105°C at 0, 6, 12, 24, 36 and 48 hours have been measured.

The main goals of this research are obtaining, bleaching in two stages, thermal ageing and evaluating of brightness and yellowness properties of CMP hardwood.

The experimental results of this study shows that the obtained CMP hardwoods could be added to papers for printing, graphic and packaging industry for increasing of printing properties (printability), adhesion of inks and varnishes and optical properties (opacity) of papers.

Key words*: hardwood, chemical mechanical pulp, bleaching, thermal ageing, fiber materials*

INTRODUCTION

The *Populus* are fast-growing species trees. Reaches a height of about 25m and live up to 400 years. The Poplar wood finds wide application for the production of fibrous materials, and the advantage is that theъ are grown easily and well adapted to soil and climatic conditions of our country [1, 2].

Poplars are found in warm and low parts of our country. In Bulgaria meet basic 4 types of poplar: white poplar (*Populus alba*), black poplar (*Populus nigra*), gray poplar (*Populus canescens*) and aspen (*Populus tremula*) [3-5].

Of all the physical properties of wood most important is density. From her depends on the quantity of expenditure in digesting liquid [6, 7].

EXPERIMENTAL

Chemical mechanical pulps (CMP) are obtained from the fast-growing hardwood poplar wood from species *Populus deltoids cultivar Hunnegem*. During the process of production of CMP are used: Na_2SO_3, analytical grade, NaOH and H_2O_2. During the bleached are utilized: H_2O_2, analytical grade, Rongalyte C ($NaHS_2.CH_2O.2H_2O$), from BASF. The initial material for laboratory experiments is a Poplar

Populus

wood, characterized by higher cellulose content, lower lignin content and higher density.

The reagents Na_2SiO_3 and $MgSO_4$ were applied as stabilizers of the H_2O_2. NaOH was added to reach a pre-determined pH level (10.5) [2, 5].

The following parameters of the produced CMP have been determined:

- Yield [%], determined by weight method in comparison to the mass of the absolutely dry timber;

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- Milling degree, as determined by the device Schopper – Riegler (°SR) as per EN ISO 5267 – 1/AC:2004;
- Microscopic images of the CMP. Used a light microscope OLYMPUS BX 53.

For all used fibrous materials the degree of Brightness R457 and Yellowness (ISO 2470:2002) was determined before and after ageing thanks to the appliance by Spectrophotometer Gretag Magbeth Spectroeye.

Production of CMP

Wood cleaned from the root part and later shredded into slices with 20mm thickness. After roots removal the wood was chopped into chips of standard dimensions of 15x20x3mm. Used poplar wood species Populus deltoids cultivar Hunnegem is 100g in absolutely dry fibrous mass [5].

Obtained two types chemical mechanical pulps:

- CMP of Type 1 is obtained with 8% NaOH and 5% Na_2SO_3;
- CMP of Type 2 is obtained with 8% NaOH, 5% Na_2SO_3 and 2% H_2O_2.

The CMP of Type 1 and 2 were received under the same conditions of temperature (80°C), hydromodul ratio 1:5, duration of process 120 min etc.

The preliminary weighted chips have been placed in a thermostatic container with the aim to temper it and to maintain the required permanent temperature.

After retention for a specified period, the used solution was removed and the chips have been washed to reach pH=7. The treatment continued by chips refined in a Sprout-Valdron laboratory mechanical refiner. Further fiber materials it was washed away and sorted out manually between two sieves.

The yield of CMP is calculated by the mass method. After soaking for 24 hours in distilled water, the treated chips were washed to reach neutral pH and dried into a drying apparatus at 105°C to achieve absolute dry state.

Bleaching of fibrous materials

First stage of bleaching – with 2% H_2O_2:

During the first stage of whitening pH=10.5 and it is maintained thanks to additives like: NaOH 2%, Na_2SiO_3 5%, $MgSO_4$ 0.5%. In order to sequester the ions of the heavy metals - solution of EDTA (ethylenediaminetetraacetic acid) was utilized. The quantities of all reagents are expressed as percentage regarding the absolute dry fibrous material. Separately prepare bleaching solution as a final H_2O_2 was added and the solution was stirred to homogeneity. The fibrous materials is placed in a polyethylene bag. The content of the bleaching solution is poured at mass for bleaching. During the process, the mass is mix periodically. After the completion of the first stage, the fiber material is washed properly to obtain pH 7 and in this manner it is able to undergo the next phase. The conditions of bleaching are given in Table 1.

Table 1. Conditions of bleaching CMP

Type of Bleaching	Quantity of reagent, (%)	T, (°C)	Duration of process, (min)	Concentration of fibrous materials, (%)	pH of the solution
I stage	2% H_2O_2	70	120	10	10.5
II stage	1.5% Rongalyt C	70	60	6	5

Second stage of bleaching - Rongalite C

The conditions of the bleaching in the second stage are presented in Table 1. During the second stage of whitening of the two fiber materials, the reagents utilized are Rongalyt C 1.5% and EDTA 0.5%. The process of bleaching is similar to the one described in the first stage. After completion of the process, the fibrous mass is washed away again to adjust pH 7.

Ageing of fibrous materials

High-yield fibrous materials contain a lot lignin and therefore faster ageing. Samples of unbleached and both bleached (single-step and two-step) fibrous materials. Obtained are samples which are dried under natural conditions in the dark, without interference by direct sunlight. After drying the samples are subjected to artificial thermal aging at 105°C. In order to characterize the ageing process for bleached and unbleached samples, the degrees of brightness and yellowness for periods of 0, 2, 4, 6, 12, 24, 36, 48 and 72 hours since the commencement of the artificial thermal ageing are determined.

Microscopic analysis of the fiber material

After obtaining, bleaching and ageing CMP were taken microscopic pictures of apparatus OLYMPUS BX 53. Microscopic analysis was made on the requirements of ISO 8658-71. Prior to this a small amount of each sample was treated to produce a fibrous materials, which was then treated wich distilled water aiming to obtain a homogeneous suspension of a concentration of 0.05%. After drying of samples is added solution of Cl-Zn-J (Herzberg reagent) in ISO 9184-3:1990.

Table 2. Chemical and physical properties

Wood	Density in air dry state, [kg/m^3]	Cellulose, [%]	Lignin, [%]
Populus deltoids cultivar Hunnegem	504	50.4	21.2

RESULTS AND DISCUSSION

The results of the chemical analysis and physical characteristics of the used wood of the species *Populus deltoids cultivar Hunnegem* are presented in Table 2.

From the data in the Table shows that the test species poplar is characterized by much higher density than the usual (about 300-350 kg/m^3) known species of poplars in Bulgaria. It differs with higher quantity of cellulose than 50% and lignin about 20%. This shows that this type poplar is suitable for obtaining HYFM and its use in the composition of different types of papers and cardboards.

During the study we obtained CMP type 1 - yield is 90% and degree of milling was 13^{0}SR, CMP type 2- yield is 88% and degree of milling is 14^{0}SR.

The utilization of HYFM in various brands of paper and cardboard is limited because of the low level of whiteness. Therefore, the resulting chemical mechanical pulp is bleached in two stages.

For CMP type 1 degree of whiteness has increased by about 20 units. Almost the same result was obtained for the other CMP type 2 about 21 units (fig. 1-4).

The degree of yellowness in CMP Type 1 has decreased about 12 units of type 2 about 14 units. It is seen that in the process of aging as time went on, the degree of whiteness decreases and the degree of yellowness increases in all samples.

Furthermore artificial thermal ageing at 105ºC is conducted. In order to investigate the impact of this ageing over the parameters of the different fiber materials, bleached and unbleached ones, the levels of whitening and yellowness are measured after various periods of time 0, 6, 12, 24, 36 and 48h. The most intensive in the process of artificial thermal aging change is observed in the early in the process.

On Figs 1 and 2 show the kinetic patterns that show the change of the degree of whiteness and yellowness over time for CMP type 1.

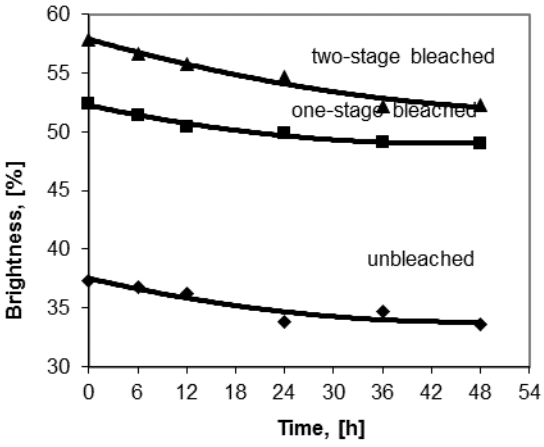


Fig. 1 Change of the degree of Brightness with time from CMP type 1

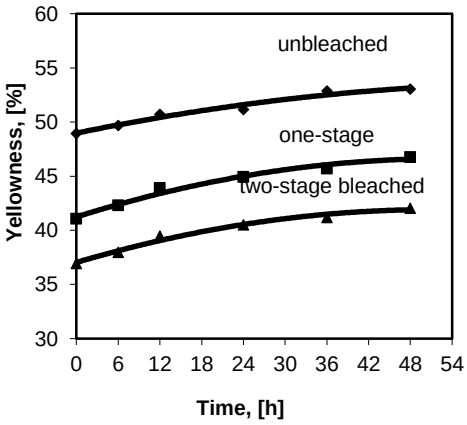


Fig. 2 Change of the degree of Yellowness with time from CMP type 1

From Fig. 1 it can be seen that the degree of whiteness decreases in all fibrous materials, regardless of whether it is unbleached, bleached in two stages or one stage, but to varying degrees. The higher degree of whiteness in the aging process is retained in a two-stage bleached materials.

Fig. 2 shows that regardless of the type of the test samples (bleached or unbleached), yellowness increases with time. Less increase in the degree of yellowness was observed in a two-stage bleached pulp - about 4 units.

In Fig. 3 are observed the same tendencies. The difference here is that the receiving of CMP type 2 it is treated with H_2O_2 and another in unbleached type this mass is a degree of whiteness 42.59%. The mass is about 5 units higher brightness compared with CMP type 1.

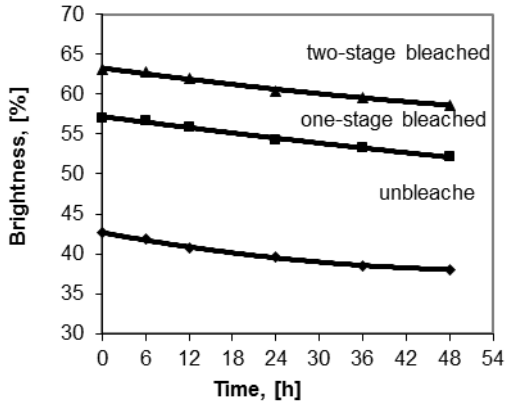


Fig. 3 Change of the degree of Brightness with time from CMP type 2

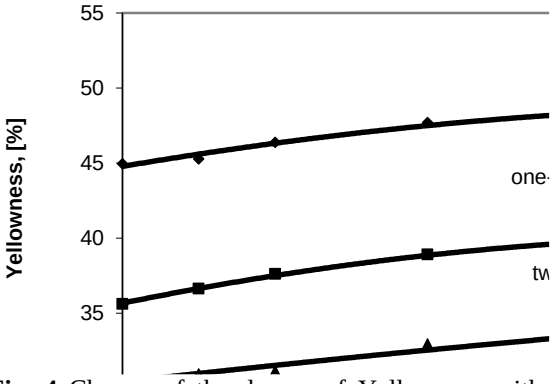
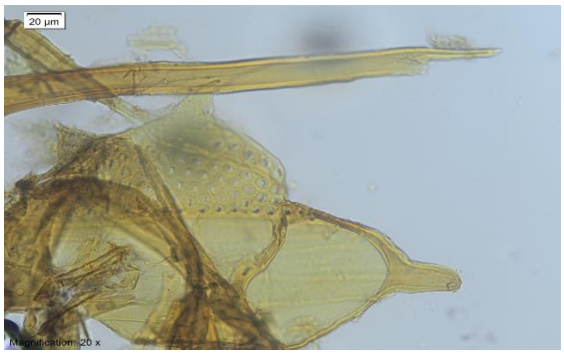


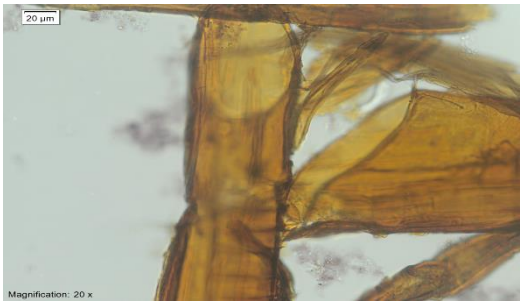
Fig. 4 Change of the degree of Yellowness with time from CMP type 2

Fig. 4 shows the degree of yellowness increases with time in all samples. From figure 2 and Fig. 4 shows the degree of yellowness increases with about 4-6 units, regardless of how it is obtained the mass, whether bleached or unbleached. Fig. 1 and 3 it is seen that when using the bleaching reagent, in this case H_2O_2, another during the actual obtain the CMP, to increase the degree of whiteness of unbleached CMP (type 1 and 2) by approximately 5 units (from 37.37 to type 1 to 42.59 with type 2). The degree of yellowness of the two types CMP are: CMP type 1- 48.95% and CMP type 2 - 44.95%. Of fibrous material from CMP type 1 and CMP type 2 unbleached and two stage bleached type made microscopic images.

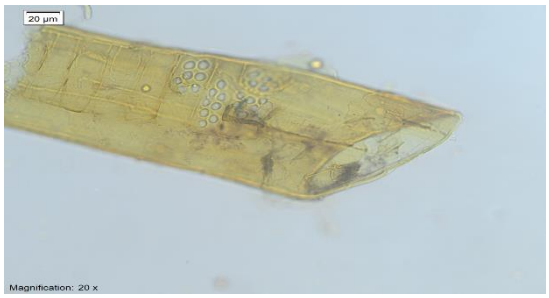
Picture 1. Unbleached CMP type 1



Picture 2. Two bleached CMP type 1



Picture 3. Unbleached CMP type 2



Picture 4. Two bleached CMP type 2

From microscopic images from CMP visible characteristic structural elements of hardwood. There was no difference in the microscopic analysis of fibrous materials in unbleached, bleached a one or two stage types. Perhaps the two stage bleached mass see a chopped fiber or twisted more and more jagged edges (pictures 1 - 4).

Observed typical HYFM - rough and uneven. They can see the another typical hardwood elements and torn fibers. These ruptures are obtained most likely by – rafined размилане milling or at the very chemical treatment of the

wood during their transformation into a fibrous materials. There are typical dishes with open ends that have the extended typical of the hardwood.

CONCLUSIONS

- *Populus deltoids cultivar Hunnegem* of fast growing species wood, with density of 504 kg/m^3 and rich carbohydrate portion, cellulose (50.4%) and lignin (21.2%). It is therefore suitable for obtaining of high yield fibrous materials.
- Obtained two types of works (type 1 and type 2). Type 2 is used in H_2O_2 at the receiving of the table, and type 1 without H_2O_2 (other things being equal). Yield CMP type 1 is 90% and degree of milling - 13^{0}SR and extraction of CMP type 2 - 88%, and the degree of milling - grinding is 14^{0}SR.
- Because of the low level of brightness, the CMP was treated by two-stage bleaching. During stage I the agent utilized was an H_2O_2, while during stage II reduction agent was applied - Rongalyt C. The final degree of brightness achieved for CMP type 1 (57.88%) and CMP type (63.15%). The obtained CMP has good optical properties and they can be used in the composition of even higher quality types of paper and paperboard.
- From microscopic photographs show typical structural elements typical of the hardwood. In some parts have chopped fibers, twisted or those with jagged ends.

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ПОЛУЧАВАНЕ НА ВИСОКОДОБИВНИ ВЛАКНЕСТИ МАТЕРИАЛИ ОТ ШИРОКОЛИСТНА ДЪРВЕСИНА И ОЦЕНКА НА ТЕХНИТЕ ОПТИЧНИ СВОЙСТВА В ПРОЦЕСА НА ТЕРМИЧНА ОБРАБОТКА

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(Резюме)

Основните влакнести материали използвани в целулозно-хартиената промишленост са: целулоза, полуцелулоза, високодобивни влакнести материали и вторични влакнести материали. Всички те са от растителен произход. Получават се основно от дървесина и едногодишни растения.

В това изследване е използвана тополова дървесина от вида *Populus deltoids cultivar Hunnegem* с повишена плътност (504kg/m^3). Получени са два вида химико-механични маси (ХММ). ХММ тип 1 е получена само със 7% NaOH и 5% Na_2SO_3, а ХММ тип 2 със 7% NaOH, 5% Na_2SO_3 и с 2%H_2O_2, при еднакви други условия – температура, хидромодул, продължителност на процеса и т.н.

Двете ХММ са с ниска степен на белота и затова след това са избелени двустепенно. При първа степен избелването е проведено с H_2O_2, а на втора степен с Rongalyt C. След това е проведено е изкуствено термично стареене при 105^{o}C. Проследена е промяната в белотата и жълтината при термично стареене от 105^{o}C на 0, 6, 12, 24, 36 и 48 час.

Целта на настоящата работа е получаване в лабораторни условия на химико-механични маси от широколистна дървесина, последващо двустепенно избелване и проследяване на изменението на белотата и жълтината с течение на времето при термично стареене от 105^{o}C.

Експерименталните резултати от това проучване показват, че получените ХММ от широколистни дървесни видове могат да бъдат добавени в състава на хартиите за полиграфичната и опаковъчна промишленост. Те подобряват печатните свойства, адхезията с мастила, лакове и оптичните свойства (непрозрачност) на хартиите.