A tépési mutató értékei a fehérítés hatására 20-22%-kal javulnak. A 80% névleges fehérségű búzaszalma cellulóz tépési mutatója 5-6,5 mNm^2/g tartományban változik, az évjárattól és a technológiai paraméterektől függően. A legjobb fehérségű energiafű rostnál (E3/2) ez az érték 8,5 mNm^2/g, mely azt jelenti, hogy az E3 energiafű fehérrost tépőszilárdsága a szalmacellulóz tépőszilárdságánál lényegesen jobb.

Összefoglalás, konklúziók

Az eddigi eredmények alapján az alábbi következtetések vonhatók le:

- az energiafüvekből mind fehérített, mind fehérítetlen cellulóz előállítható,
- a granulometriai, fizikai és optikai vizsgálatok alapján megállapítható, hogy a legjobb minőségű cellulóz az E3 mintából állítható elő,
- a kísérleti eredmények alapján 1 t energiafű tömegének 1/3 részéből válhat papíripari alapanyag, és kb. 60-65%-ából nyerhető hőenergia,
- az energiafüvekből nyert rostok alkalmasak csomagoló- és író-, nyomópapírok előállítására is.

A szerzők köszönetet mondanak az OM Alapkezelő Igazgatóságának a munka elvégzéséhez nyújtott anyagi támogatásért.

Summary, conclusion

Based on the results achieved so far following conclusion can be established:

- Both bleached and unbleached pulp can be made from energy grasses
- Granulometric, phisical and optical test show that the highest quality pulp can be made from sample marked E3
- Results of the trials show that 1/3 part of 1 ton of an energy grass can be transfered into paper intustrial raw material and about 60-65% can be used as heat energy
- fibres gained from energy grasses are suitable to make wrapping and printing and writing papers.

Zusammenfassung, Folgerungen

Folgende Folgerungen können aufgrund der bisheringen Ergebnisse abgezogen werden:

- Energiegrasarte sind für die Herstellung von gebleichten sowohl von ungebleichten Zellstoffen geeignet
- Granulometrische, physische und optische Untersuchungen zeigen, daß die höchste Qualität von Muster E3 hergestellt werden kann
- Die Testergebnisse beweisen, daß 1/3 Teil von Tonnen Energiegrasart zum Rohstoff für die Papierindustrie überführht wird und von etwa 60-65% kann Heizenergie produziert werden
- Die Faser aus Energiegrasarten sind auch zur Herstellung von Packungspapieren und Schreib- und Druckpapieren geeignet.

ETO: 577.152:676.014.82:676.024.61.04:676.017.3:676.017.62:676.164.3
Keywords: enzymatic treatment,
chemical properties, morphological properties

Effect of enzymatic treatment of cellulose fibres on their chemical and morphological properties

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Introduction

The application of biotechnological processes in pulp and paper industry began in the middle of 70-ties of the last century. The first trials were made with fungi producing enzymes, which were used in the chip treatment. It was a long lasting procedure and gave irreproducible results. The wider use of enzymes to improve manufacturing processes in global and particularly in cooking, bleaching and refining has began since the end of 80-ties.

Enzymes being produced on an industrial scale are available at relatively low price.

Az alábbi közlemény magyar nyelvű változata a Papíripar 2002/4. számának 131. oldalán található

Producer of enzymes	Enzyme
Trichoderma reesei	Liftase A40
Trichoderma Lagibrachiatum	Pergalase A40
Aspergilus niger	Cytolase 123

Table 1 The origin of cellulase and hemicellulase enzymes used for improving sheet-formation properties

Hydrolytic enzymes (cellulase, hemicellulase) have been found to be commercially feasible for improving sheet-forming properties and bleachability of different pulp.

In my present contribution I am dealing only with the cellulase enzyme. My paper is divided on three parts. In the first part the effect of the cellulase enzyme on the chemical properties of different cellulose fibres are discussed. In the second part effect of enzymatic treatment on the colloidical and morphological properties of the fibres are highlighted and finally in the third part of the contribution some results achieved with enzymatic treatment on the paper properties are shown.

The cellulase enzyme first used in the practice has a complex character and has three parts acting differently. All three parts of enzyme act on the amorphous region of cellulose macromolecule yielding different end product.

The cellulase enzyme can be produced by different organisms,among them fungi and bacteria also are existing.

Some typical enzymeproducer organism and the name of the enzyme are put on the table 1.

According to the literature usual conditions for enzyme treatment of pulp suspension are as follows:

- Ezyme dosage 0,2-0,4%;
- pH 4,8-6,2;
- pulp consistency 1,5-5,0%;
- temperature of treatment 40-50°C;
- duration of treatment 30-60 minute.

Some exact condition of the enzymatic treatment and author of the article are given in Table 2.

Enzyme dosage	pH	Consistency%	Temp. °C	Duration, min	Author
0,2-0,4%	6.2	3	40	60	Sarkar et al. (1995)
0,1%	4.8	3	50	30	Pommier et al. (1989)
0,2%	6.0	3	40-45	30	Pommier et al. (1990)
0,4 U/g	4.8	3	40	30	Jackson el al. (1993)
0,2-0,4%	5.0	1,5	50	30	Kantelinen el al. (1997)
?	4.8	2	50	60	Oltus et al. (1987)
0,2	5.0	5.0	50	30	Nishi el al. (1996)

Table 2. Usual condition in enzyme treatment of pulp

Experimental part

In the first series of experiment different virgin pulps were treated with enzyme and the changes in chemical properties were investigated. In this case a special pure enzyme purchased from Aldrich-Sigma company was used. This enzyme requires a slightly acidic medium (pH 4,8-5,0). For the preparation of the pulp slurry of appropriate pH citric puffer and distilled water were used. Other conditions of enzymatic treatment are given in Table 3.

Enzyme:	Aldrich Sigma cellulase/xilanase 70/30:
Fibre:	different virgin fibres
Dosage:	0,2% based on oven-dry substrate
Tempereture:	50°C
Time:	60 min.
Pulp consistency:	50g fibre/l

Table 3. Conditions of enzyme treatment

After the enzymatic treatment pulp slurry was diluted with distilled water and washed via metallic wire. Before enzymatic treatment and after it the following parameter were measured:

- Loss of mass %;
- glucose content in the reaction's medium;
- alkaline solubility in 1% NaOH;
- aldehyde groups
- iodine sorption by cellulose;
- average degree of polymerisation.

These parameters are shown in Table 4.

It can bee seen that mass losses in all cases are the same that is about 3,3-3,8%. The glucose content in case of filter paper and TCF kraft pine pulp almost similar but in case of birch pulp is formation of glucose is much less. The alkaline solubility also increases after enzymatic treatment except of birch pulp.

The most interesting functional group of cellulose namely aldehyde groups are also increased very significantly in case of filter paper, while aldehyde groups in birch pulp didnot change.

	filter paper		**TCF kraft pine pulp**		**TCF kraft birch pulp**	
	untreated	treated	untreated	treated	untreated	treated
Loss of mass, %	0	3.32	0	3.36	0	3.84
Dissolved glucose by treatment, mg/l	0	195	0	170	0	35
Alkaline solubility, %	3.42	4.67	2.86	3.84	5.35	5.83
Aldehyde groups, %	0.0186	0.0620	0.0372	0.0496	0.0744	0.0775
Iodine sorption, mg I/g	117.00	106.83	129.75	104.30	167.10	140.63
Average DP (in Cadoxen)	1450	745	1200	730	1020	815

Table 4. Effect of enzyme treatment on chemical properties of different virgin fibres

The accessibility of cellulose can be characterised by measuring of iodine sorption. It can be seen that due to enzymatic treatment – as enzyme act preferably in the amorphous region – accessibility measured by iodine sorption decreased in all cases. The degree of polymerisation also decreased very significantly, in case of filter paper by 50%, in case of pine pulp by 30-35%, in case of birch pulp by 20%.

It is well know from the literature data, that enzyme treatment can improve drainage properties of pulp lowering at same time freeness of the suspension. It is agreed that enzyme act as a razor, cleaning the fibre surface from the fibrils and other small particle existing on the fibre surface. In this respect it was interesting to know how does act the enzyme on the pure, virgin pulp of different degree of beating.

For this purpose two types of pulp one unbleached long fibre (sulphate spruce) and a bleached short fibre (sulphate poplar pulp) were beaten in the laboratory Valley-beater in the broad limit of °SR (20 to 85 °SR) than the beaten pulp was treated by enzyme and after the treatment some parameters were measured. The same parameters were established in pulp beaten in different level without enzyme treatment.

The following parameters were measured:

- freeness in °SR;
- drainage time;
- water retention value;
- fine content;
- specific surface;
- reducing sugar
- and fine losses due to enzymatic treatment.

The condition for the enzymatic treatment were as follows:

- pH:5,0;
- temperature 50°C;
- duration 60 min.;
- enzyme dosage 0,3% Pergalase A 40 (activity 2700 IU/g);
- pulp consistency 3,5 %.

The **Table 5.** shows summarised results of the enzymatic treatment of differently beaten pulp.

Decrease of freeness due to enzymatic treatment is shown in Figure 1.

It can bee seen that more changes in °SR are in case of unbleached spruce pulp in the medium range of beating, it means 10 °SR but in the region of high beating it is 15-20 °SR, while in case of poplar pulp the change is no more than 5 °SR.

Changes in the drainage time due to enzymatic treatment are shown in Figure 2.

It is clear from the Figure 2. that enzyme treatment reduces drainage time very significantly, the

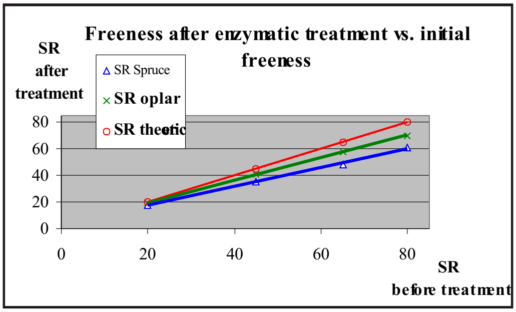

Figure 1.

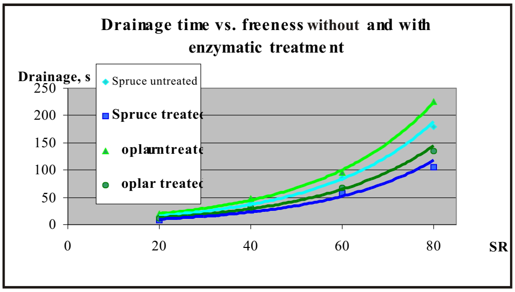

Figure 2.

Parameters	Unbleached spruce sulphate pulp								Bleached poplar sulphate pulp							
Enzyme:	no	yes	no	yes	no	yes	no	yes	no	yes	no	yes	no	yes	no	yes
Freeness, °SR	20	18	45	35	62	42	80	65	23	21	43	38	69	64	84	79
Drainage time, s	15,2	8,2	43,7	31,0	79,3	38,8	183,9	70,4	16,1	11,0	47,8	30,0	124,0	73,80	298,8	137,0
WRV 900g, 30 min	283,1	261,5	364,0	310,0	375,3	332,5	417,8	388,8	304,1	280,5	376,6	364,0	409,0	397,0	453,4	443,7
Fine content, % (DDJ wire 200 mesh)	8,16	6,60	10,24	7,34	14,76	7,72	23,84	13,4	20,1	17,4	41,3	30,6	52,1	39,9	72,8	62,2
Specific surface, m^2/g (methylene blue)	26,1	24,6	36,9	28,0	40,6	29,4	44,2	27,9	26,2	23,5	35,7	32,4	56,8	55,0	65,5	64,3
Reducing sugar, mg/l (by DNS)		1,0		3,28		4,85		6,43		2,28		3,80		5,14		6,09
Fine losses due to enzyme treatment, mg/g		15,6		29,0		70,1		105,0		27,0		106,0		122,0		105,5

Table 5. Characteristics of cellulose fibres before and after enzymatic treatment at different SR°

highest reduction is achieved in case of poplar pulp. The more the drainage time after the beating the more reduction can be achieved by enzymatic treatment.

Due to the enzymatic treatment the water retention value, specific surface and fine content are also decreased.

The biggest changes due to enzyme action can be seen in specific surface and in fine content. Especially in case of unbleached spruce pulp specific surface and the fine content have been changed. In case of poplar pulp the differences are not so much.

The generation of reducing sugar is also increased as the degree of beating becomes more. It is again an evidence, that during the beating the surface of cellulose fibre enlarges and becomes more accessible to the action of the enzyme. By this phenomena decrease of fine content and specific surface of enzymatically treated pulp can be explained.

The accessibility of cellulose fibres depends on the pore structure, the pore dimensions and pore volume as well. In order to establish the changes in pore structure of cellulose fibres due to enzymatic treatment, the pore dimension and pore volume of cellulose fibres beaten at different beating level and enzymatically treated were

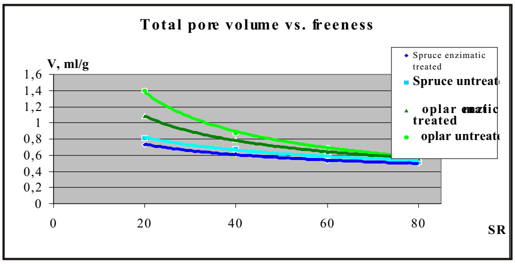

Figure 3.

measured using a mercury pressure porosimeter type Carlo-Erba.

On the porosimeter the total pore volume, volume of micro-pores, volume of macro-pores and the average pore radius of micro- and macro-pores were measured. A pore measurements were performed on the handsheets made from differently beaten pulp before and after enzymatic treat-ment. Sheets were made on the Rapid-Köthen sheetformer from spruce and poplar pulp.

The results are summarised in **Table 6.-7.** and **Figure 3.-4.**

Enyzme dosage	Freeness, °SR	Total pore volume ,cm^3/g	Volume of macro-pores, cm3/g r>7,5 m	Volume of micro-pores, cm3/g r<7,5 m	Average pore radius R_{av}, m	
					macro	micro
-	23	1,284	0,533	0,751	10,6	6,68
+	21	1,047	0,387	0,660	12,6	6,68
-	43	0,820	0,259	0,561	12,7	3,34
+	38	0,800	0,272	0,528	12,9	3,36
-	69	0,650	0,204	0,446	16,3	1,76
+	64	0,630	0,206	0,424	16,7	1,43
-	84	0,546	0,208	0,338	12,9	1,2
+	79	0,523	0,214	0,309	16,9	0,81

Table 6. Pore structure of poplar pulp sheets at different SR° with and without enzymatic treatment

Enyzme dosage	Freeness, °SR	Total pore volume ,cm^3/g	Volume of macro-pores, cm3/g r>7,5 m	Volume of micro-pores, cm3/g r<7,5 m	Average pore radius R_{av}, m	
					macro	micro
-	20	0,812	0,394	0,418	31	6,7
+	18	0,757	0,333	0,424	11	0,8
-	46	0,697	0,340	0,357	32	1,4
+	35	0,642	0,265	0,377	10,5	1,7
-	62	0,560	0,222	0,338	23	1
+	42	0,607	0,243	0,364	12	1,4
-	82	0,540	0,263	0,277	12	1
+	65	0,521	0,227	0,294	10,2	1

Table 7. Pore structure of spruce pulp sheets at different SR° with and without enzymatic treatment

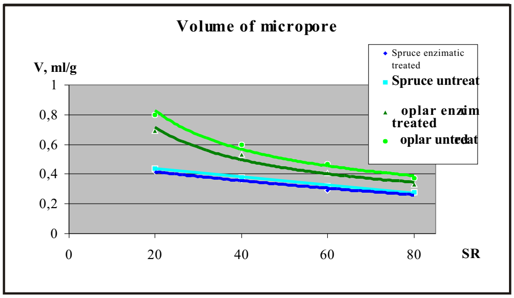

Figure 4.

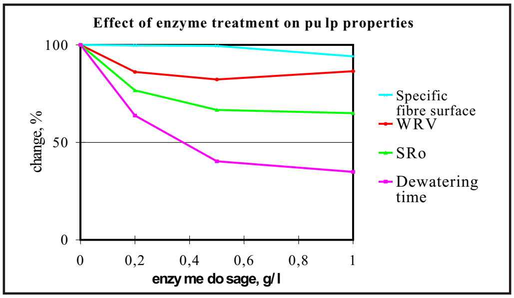

Figure 5.

Enzyme:	Pergalase A40
Fibre:	high rate secondary pulp
Consistency:	30 g/l fibre
Dosage:	0.2, 0.5, and 1.0 g/l enzyme in the water
Temperature:	50°C
Time:	30 min.

Table 8. Conditions of enzyme treatment

Generally it can be said that pore structure changes more significantly due to the beating that due to the enzymatic treatment. Pore volume (macro- and micro-pores) changes more than its dimension. Pore volume of poplar pulp has changed more than spruce pulp. Due to enzymatic treatment total pore volume changes more at the beginning of the beating. The same is seen on the figures 3. and 4.

As the beating became stronger the differences between pore volume of untreated and enzymatically treated pulp has been smaller. It can be explained again by the accessibility of enzyme molecules onto fibre surface or inside the pores which decreases with the extent of beating.

The industrial utilisation of enzymatic treatment became interesting when problem arised concerning the improving papermaking properties and runnability on one of PM producing bag paper from high rate secondary fibres in the furnish.

To solve this problem an enzymatic treatment was planed. In this case first of all the dosage of enzyme was the most interesting parameter. It is known from the literature that an over-dosage of enzyme can damage paper properties so the right dosage is necessary to know.

A lab scale treatment was performed to establish the action of enzyme on the paper properties. The condition of the enzyme treatment is shown on **Table 8.**

The pH of the pulp before enzymatic treatment was adjusted to 4,8-5,0 by adding appropriate amount of H_2SO_4.

The pulp properties measured after enzymatic treatment are shown on the **Figure 5.**

It can be seen that the biggest changes occurred in the beginning namely at the smallest enzyme dosage (0,2% on oven dried pulp).

Freeness and drainage time decreased more than WRV and specific surface. In respect of runnability of the PM these two parameters (freeness and drainage time) are more significant. What the physical properties of the paper produced from enzymatically treated pulp are concerned small amount of enzyme does' not decrease the breaking length, tear and burst more than 5-8% but the air permeability which is the important parameter for the bag paper improved very significantly as it can be seen on Figure 5.

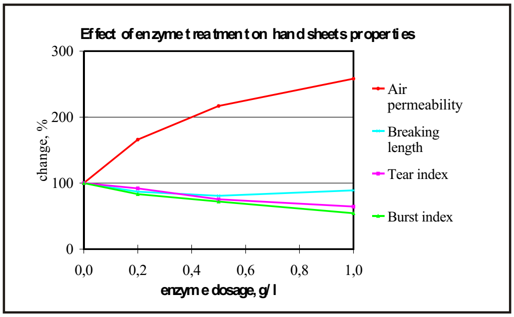

Figure 6.

Summary

A cellulase enzyme (Pergalase A 40 Genecor) was used to investigate its action on chemical, morphological and papermaking properties of cellulose fibres of different origin.

It was established that cellulase enzyme as an hydrolysing agent can cause big changes in the chemical properties of pure cellulose (filter paper, TCF pine pulp and TCF birch pulp). Enzyme causes decrease of accessibility measured by iodine sorption, it increases alkali solubility, produces glucose in filtrate, drops the DP of cellulose molecule by 30-50%, increases amount of reducing end groups.

Enzymatic treatment of differently beaten pulp yields significant drop of °SR, drainage time, decreasing of specific surface and fine content, at the same time it facilitates the drop of pore volume, pulp became less porous and more compact.

Utilising enzyme in near industrial conditions for the production of bag paper, 2 kg/t enzyme dosage improve runnability and drainage of pulp and increase of permeability of paper with only a small decreasing of strength properties.