

SEPARATING, CHARACTERIZATION AND APPLICATION OF ALFA GRASS (*Stipa tenacissima*) CHEMICAL COMPONENTS

1. PULPING OF ALFA GRASS WITH FORMIC ACID/ACETIC ACID MIXTURE

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(Reçu le 24 Février 2009, accepté le 19 Mai 2009)

ABSTRACT: The pulping of Alfa grass at atmospheric pressure using a mixture of formic acid/acetic acid/water was investigated. Different pulping variables were studied, especially the percentage of formic acid, acetic acid and water, pulping time, the liquor to fibre ratio and impregnation time. The obtained unbleached pulps were analysed in accordance with the Kappa number and the degree of polymerisation. The delignification of unbleached pulp was realised by using peroxyacids in acidic organic medium and hydrogen peroxide in alkaline medium.

Key words: Alfa, pulping, formic acid, acetic acid, delignification, bleaching.

RESUME: La cuisson de l'Alfa est réalisée sous la pression atmosphérique au moyen d'un mélange acide formique/acide acétique/eau. L'optimisation de cette cuisson est réalisée suite à l'étude des effets de quelques paramètres physico-chimiques dont principalement la composition du réactif de cuisson, la durée de cuisson, le rapport liqueur/matière sèche et l'imprégnation. La pâte écru est caractérisée par l'indice Kappa et le degré de polymérisation. Le blanchiment de la pâte écru est réalisé par un traitement aux peracides en milieu acide organique suivi d'un traitement par le peroxyde d'hydrogène en milieu alcalin.

Mots clés: Alfa, cuisson, acide formique, Acide acétique, délignification, blanchiment.

INTRODUCTION

Alfa grass (*Stipa Tenacissima*), also named Esparto grass, is extensively cultivated in semi-arid and arid regions in the north-west Africa and southern Spain. It is a well-known plant used as a source of paper pulp which is generally used in the manufacture of printing papers [1-3]. Recently various chemical surface treatments have been performed on the Alfa fibre in order to obtain a new family of reinforcers in composite materials [4-5]. Obtaining cellulose fibres from Alfa grass using the traditional Kraft procedure consists of degrading a large amount of lignin and hemicelluloses and making them soluble in the alkaline medium. The specific properties of black liquor resulting from soda cooking make it difficult to carry out the concentration/combustion process and usually no alkali recovery was realized after pulping.

During the past few years various new technologies have been developed for separating the chemical components of vegetable matter without combustion of the cooking liquor [6-9]. The lignin and sugars can be isolated and the cooking agents are easily recyclable. Delmas and co-workers [9-12] have reported an original type of cooking carried out at atmospheric pressure, at relatively low temperature and using a mixture of formic acid, acetic acid and water.

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This process is easily adapted to unbleached pulp production from different annual plants such as rice straw, the straw of triticale and wheat straw [9-12]. The numerous advantages of this procedure compared with conventional alkali pulping led us to examine the possibility of applying this process to destructuring Alfa grass. The pulping of this plant is realised by traditional alkali process and [13] to the best of our knowledge no study has been reported on separating cellulose fibres, lignin and sugars by an organosolv process.

The purpose of this paper is to report a thorough investigation on Alfa grass pulping using an organosolv process. Lignin characterization has been the subject of few reports which described the structural features of Alfa grass lignin, isolated by acidification of black liquor using the soda process [14-16]. The present study deals with a first investigation on the application of Avidel process [9], requiring mild conditions, which we have applied to Alfa grass.

EXPERIMENTAL

1 – Raw material

The pulping raw material used was Alfa grass (*Stipa Tenacissima*) came from the middle west of Tunisia. It contained 55% cellulose, 9% lignin, 31% hemicelluloses and 3.16% water as determined by the method of Van Soest and Wine (method NDF-ADE). The acetic acid (99 to 100%), formic acid (99 to 100%) and hydrogen peroxide (50 % by mass) used were commercial products (Merck).

2 – Cooking

Alfa straw was cooked in accordance with the Avidel process [9]. The cooking was carried out in a 1-l glass reactor, heated in an oil bath (107°C) at atmospheric pressure. The Alfa grass (30 g), cut into pieces with an average length of 3.0 cm, was first impregnated with the cooking liquor at 60°C for 60 minutes. After impregnation, cooking was done under various conditions as discussed later. The pulp thus obtained was first filtered, pressed and washed twice with acetic acid solution, then with water. The fibres were then screened on 65 and 100 mesh sieves using pressurised water. The under cooked pulp (rejects) was collected on the 65-mesh sieve, while the 100-mesh sieve was collected as the accept fibre, and both were dried and analysed.

The used acids were recycled by simple distillation. The addition of water to the obtained residue after evaporation of the acids, led to the precipitation of the lignin. These were filtered, then washed until neutral pH with distilled water and dried. The solubilized sugars in the water were obtained in the form of syrup after concentration.

3 – Bleaching

The unbleached pulp obtained by the cooking of the Alfa grass in a formic acid/acetic acid/water medium was bleached by means of a bleaching sequence using organic peracids as delignification agent followed by a bleaching stage using alkali hydrogen peroxide. The bleaching conditions were as follow:

- Phase 1: Bleaching in a formic acid/acetic acid medium: ratio liquor/dry matter: 8/1, ratio fa/aa: 25/75 (%v/v), quantity of hydrogen peroxide: 6% based on the dry weight of vegetable matter, temperature: 60° C and time: 1h.
- Phase 2: Bleaching in an alkali hydrogen peroxide medium: ratio liquor/dry matter: 10/1, quantity of NaOH: 4% based on the dry weight of pulp, quantity of hydrogen peroxide: 2% based on the dry weight of pulp, temperature: 90°C and time: 1h.

4 – Analysis of pulp

Chemical characteristics are measured in accordance with the following standards: Kappa number (AFNOR NF T 12-018 and T 12-019), DPv (degree of polymerisation of cellulose chain obtained by viscosity measure) (AFNOR NF T 12-005).

RESULTS AND DISCUSSION

1 – Cooking

Pulping of Alfa grass was varied according to independent parameters. The independent variables included the cooking mixture formic acid/acetic acid/water ratio, reaction time, the liquor-to-dry matter ratio, percentage of water and impregnation were studied separately. Each factor was studied in relation to pulp yield (%), residual lignin content (Kappa number) and viscosity (cm^3/g).

1 – 1 – Influence of formic acid / acetic acid ratio

Seven experiments were performed, depending on formic acid and acetic acid concentration in order to evaluate which ratio would be able to optimize the chemical characteristics of the unbleached pulp. Table I shows that, acetic acid alone was not a good delignification agent. The absence of formic acid in the medium did not allow the delignification of the vegetable matter and only rejects were recuperated (experiment 1). When using formic acid in the absence of acetic acid, the pulping of Alfa grass took place and the rejects were reduced to 0.4% but the resultant pulp was obtained with low yield and presented a low DPv (576) with a approximately low residual lignin content (Kappa number = 17.8).

Experiments 2-6 show clearly that the presence of both formic acid and acetic acid in the medium improved simultaneously the pulping yield and the Kappa number. This behaviour which was similar to that reported for other vegetable matters [10, 12], could be attributed to two separate reasons, (i) formic acid is a strong delignification agent which plays the role of the proton donor [17], (ii) acetic acid is a very good solvent of lignin and hemicellulose fragments [9].

Table I: Effect of formic acid concentration on the chemical characteristics of the pulp (Cooking conditions: temperature, 107°C; time, 3h; L/M (liquor to straw) ratio, 10/1).

Experiment Number	fa/aa/water ratio (% v/v)*	Rejects (%)	Yield (%)	Kappa Number	Viscosity (cm^3/g)	DPv
1	00/80/20	83.00	-	-	-	-
2	20/60/20	1.33	56.97	40.3	600	854
3	30/50/20	0.55	46.95	29.5	581	825
4	40/40/20	0.39	46.01	27.0	555	784
5	50/30/20	0.45	44.20	26.3	564	800
6	60/20/20	0.50	42.43	25.7	519	728
7	80/00/20	0.40	39.26	17.8	420	576

*fa: formic acid, aa: acetic acid,

The best results corresponded to a cooking liquor composition of 30% formic acid and 50% acetic acid which produced pulp with good unbleached pulp yield and viscosity.

The progressive increase in the relative amount of formic acid in this series of runs had, however, an adverse effect on unbleached pulp viscosity which can be explained by the effect of this acid on cellulose hydrolysability.

1 – 2 – Influence of cooking time

Cooking time was varied between 2 to 8 hours to evaluate the effect on pulp quality. Table II shows that increasing the cooking time reduced Kappa number and rejects yield. Kappa number reduced little after 3 h, probably due to the competition between delignification and precipitation of

dissolved lignins on the fiber surfaces [18]. Pulp yield and viscosity reached a maximum level between 3 and 4 hours and decreased slowly thereafter. Overall a cooking time of 3 h appeared optimal.

Table II: Effect of cooking time on the chemical characteristics of the pulp (Cooking conditions: temperature, 107°C; fa/aa/water ratio, 30/50/20; L/M (liquor to straw) ratio, 10/1).

Experiment Number	Time (h)	Rejects (%)	Yield (%)	Kappa Number	Viscosity (cm ³ /g)	DPv
8	2	9.16	42.39	36.4	520	728
3	3	0.55	46.95	29.5	581	825
9	4	0.44	47.43	27.3	600	855
10	8	0.35	42.65	23.2	548	773

1 – 3 – Influence of the L/M ratio

Various liquor/dry matter ratios (from 8/1 to 15/1) were chosen to determine the impact of this factor on delignification and pulp quality (Table III).

Table III: Effect of the L/M ratio on the chemical characteristics of the pulp (Cooking conditions: temperature, 107°C; time, 3h; fa/aa/water ratio, 30/50/20).

Experiment Number	L/M Ratio	Rejects (%)	Yield (%)	Kappa Number	Viscosity (cm ³ /g)	DPv
11	8/1	8.00	42.43	38.3	549	774
3	10/1	0.55	46.95	29.5	581	825
12	12/1	0.14	45.52	28.5	557	787
13	15/1	-	45.83	26.2	609	896

It can be seen from Table III that the effect of L/M ratio on pulp yield rejects level, and Kappa number, is considerably significant. Increasing the L/M ratio from 8/1 to 15/1 resulted in a considerable reduction in Kappa number (12.1 units) and rejects. A high L/M ratio contributed Alfa hydrolysed products to the cooking mixture and to make soluble hemicelluloses and lignin fragments. These results are in agreement with those obtained by Delmas and coll. [18]. However, cooking with a high L/M ratio (experiment 13) implied important energy consumption for recycling the acids, consequently increasing the cost of the transformation of Alfa into paper pulp. An L/M ratio of 10/1 (experiment 3) would be suitable to perform Alfa cooking based on these laboratory tests.

1 – 4 – Influence of the cooking liquor water

Table IV shows that the water content in the cooking medium is an important parameter in pulping of Alfa. It has an effect on organic acid dissociation and hydrolysis of hemicelluloses, but it is a very bad solvent for lignin. The best result was obtained when using fa/aa/water: 30/50/20 composition which led to unbleached pulp with Kappa number 29.5 in 47% yield.

Table IV: Effect of the cooking liquor water on the chemical characteristics of the pulp (Cooking conditions: temperature, 107°C; time, 3h; L/M (liquor to straw) ratio, 10/1).

Experiment Number	fa/aa/water ratio (% v/v)	Rejects (%)	Yield (%)	Kappa Number
14	30/70/00	7.00	47.76	37.7
15	30/60/10	1.24	36.80	36.8
3	30/50/20	0.55	46.95	29.5
16	30/40/30	0.66	46.44	30.5
17	30/30/40	0.71	45.62	34.4

Beyond this optimised water content, delignification decreased (Kappa number increased, see table IV). Accurate quantity is therefore important to obtain a maximum delignification.

1 – 5 – Influence of the impregnation stage

Before performing the pulping, the Alfa grass should be impregnated, in a first stage, by means formic acid/acetic acid/water (30/50/20) mixture. Effects of this impregnation treatment related to three cooking times are shown in table V. For cooking time of 2 h (experiments 8 and 18), the obtained pulps presented high amounts of rejects (respectively 9.16 and 4.20%) and a low delignification rate (Kappa number: 36.4 and 35.8). By increasing the cooking time to 3 h, the effect of the impregnation was clearly observed (experiments 3 and 19): the rejects reduced to zero and pulp yield increased. This can be explained by the fact that the impregnation stage allowed uniform penetration and diffusion of the cooking liquor chemical [18]. An impregnation stage with a cooking time of 4 h, improved the delignification of Alfa grass. The Kappa number decreased and pulp yield increased, but the pulp viscosity decreased.

Table V: Effect of the impregnation stage on the chemical characteristics of the pulp (Cooking conditions: temperature, 107°C; fa/aa/water ratio, 30/50/20; L/M (liquor to straw) ratio, 10/1, *Impregnation: 1 hour at 60°C in fa/aa/water ratio, 30/50/20).

Experiment Number	Time (h)	Rejects (%)	Yield (%)	Kappa Number	Viscosity (cm ³ /g)	DPv
8	2	9.16	42.39	36.4	520	728
18*	2	4.20	41.93	35.8	608	895
3	3	0.55	46.95	29.5	581	825
19*	3	-	49.06	28.5	617	909
9	4	0.44	47.43	27.3	600	855
20*	4	-	49.43	27.4	570	832

The experiment results showed that the best operating conditions for batch pulping of Alfa in a formic acid/acetic acid/ water environment were as follows:

- Impregnation: 1 hour at 60°C in fa/aa/water ratio, 30/50/20,
- Cooking liquor: fa/aa/water (30/50/20: v/v/v)
- Cooking time: 3h,
- L/M ratio: 10/1.

2 – Bleaching

Various bleaching process are used in order to remove residual lignin of the unbleached pulp and to eliminate the conjugated compounds responsible for unbleached pulp colour [19-20]. In this work, we studied the bleaching of unbleached pulp obtained from Alfa grass by peroxyacids in an acetic acid/formic acid/hydrogen peroxide medium. This medium presented the several advantages for the employed pulping method [21].

A preliminary delignification sequence was applied to the Alfa pulp using organic peracids followed by a bleaching stage using alkali hydrogen peroxide. This sequence was chosen because of the acidic pH of the unbleached pulp. The conditions applied and the results obtained are reported in Table VI.

Table VI shows the characteristics of pulp after first and second steps of bleaching.

- The treatment of unbleached pulp by hydrogen peroxide in organic medium led to a delignified pulp (Kappa number 15) with high selectivity, since the variation in the DPv was relatively low (DPv 884). These interesting results can be explained by the action of the hydroxonium ion OH⁺ formed during the peroxyacids stage in acidic medium:



In fact, OH^+ ion is a strong electrophilic agent which can react with residual lignin as ring hydroxylation, oxidative ring opening, substitution of side chains, cleavage of β -aryl ether and epoxidation [22].

• The action of hydrogen peroxide in alkali medium is effective in pulp bleaching. In fact the result obtained through Table VI demonstrated that an alkaline extraction carried out on a pulp 21 resulted in a considerable decrease in the Kappa number (3.7) without degradation of carbohydrates as shown by viscosity and DPv values. This can be explained by dissolving lignin fragments in alkaline medium.

Moreover the perhydroxyl anion HOO^- formed ($\text{H}_2\text{O}_2 + \text{OH}^- \longrightarrow \text{HOO}^- + \text{H}_2\text{O}$) reacted with the quinones formed during lignin degradation by peroxyacids and this induced the elimination of the last conjugated compounds responsible for unbleached pulp colour.

Table VI: Chemical characteristics of pulp during bleaching.

Pulp Number	Yield (%)	Kappa Number	Viscosity (cm^3/g)	DPv
Pulp 19 ^a	49.06	28.5	617	909
Pulp 21 ^b	45.20	15	602	884
Pulp 22 ^c	43.03	3.7	556	811

a: unbleached pulp obtained from experiment 19,

b: pulp 19 treated by peroxyacids: ratio liquor/dry matter, 8/1; ratio fa/aa, 25/75 (% v/v); quantity of hydrogen peroxide, 6% by weight in relation to the vegetable matter; temperature, 60° C; time, 1h.

c: pulp 21 treated by alkaline extraction: ratio liquor/dry matter, 10/1%; NaOH/pulp, 4%; quantity of hydrogen peroxide/pulp, 2%; temperature, 90° C; time, 1h.

CONCLUSION

The cooking of Alfa grass in a formic acid/acetic acid/water medium is very well suited for separating of vegetable matter components (cellulose hemicelluloses and lignin). However, the parameters such as: fa/aa/water ratio, cooking time and L/M ratio must be selected with care. The pulp obtained with the best conditions (fa/aa/water: 30/50/20 %v/v; time: 3 hours with 1 hour impregnation; L/M: 10/1) possessed a low Kappa number and a high viscosity, the yield of the pulp was 49.06%. The unbleached pulp obtained in this condition could be bleached in a very satisfactory approach using delignification by peroxyacids followed by bleaching by hydrogen peroxide.

Work is in progress to assess mechanical properties of this pulp and to characterise lignin and sugars.

REFERENCES

- [1] – P. Boudy, *Economie forestière nord africaine*, ed Larrose 2, Paris, **1950**, p. 777.
- [2] – A. Cerda, *J. Arid Environ.*, **1997**, 36, 37.
- [3] – G. Petroff, *Pulp and Papers Int.*, **1974**, 16, 41.
- [4] – L. Ghali, M. Zidi, S. Roudesli, *J. of Applied Sci.*, **2006**, 6, 2450.
- [5] – A. Bessadok, S. Marais, F. Gouanvé, L. Colasse, I. Zimmerlin, S. Roudesli, M. Métayer, *Composites Science And Technology*, **2007**, 67, 685.
- [6] – V. B. Diebold, W. F. Cowan, J. K. Walsh, *U. S. Patent 4.100.016*, **1978**.
- [7] – E. K. Pye, J. H. Lora, *Tappi Journal*, **1991**, 74, 113.
- [8] – J. Sundquist, *Paperi Ja Puu - Paper and Timber*, **1996**, 3, 92.
- [9] – M. Delmas, G. Avignon, *French Patent 13658*, **1997**.

- [10] – H. Q. Lam, Y. Le Bigot, M. Delmas, G. Avignon, *Ind. Crops. Prod.*, **2001**, *14*, 65.
- [11] – H. Q. Lam, Y. Le Bigot, M. Delmas, G. Avignon, *Ind. Crops. Prod.*, **2001**, *14*, 139.
- [12] – M. M. Astrid, M. B. Benjelloun, M. Delmas, R. Bravo, *Appita Journal*, **2005**, *58*, 393.
- [13] – A. Houacine, F. Pla, A. Robert, *Sonderdruck aus //Holzforschung und Holzverwertung*, **1988**, *40*, 26.
- [14] – S. Hattalli, A. Benboura, F. Ham-Pichavant, A. Nourmamode, A. Castellan, *Polymer Degradation and Stability*, **2002**, *75*, 259.
- [15] – S. Hattalli, A. Benaboura, S. Dumarçay, P. Gérardin, *J. Appl. Polym. Sci.*, **2005**, *97*, 1065.
- [16] – H. Nadji, P. N. Diouf, A. Benaboura, Y. Bedard, B. Riedl, T. Stevanovic, *Bioresource Technology*, **2009**, *100*, 3585.
- [17] – H. Q. Lam, *Thesis INPT France*, **2000**, 74.
- [18] – M. Delmas, Q. L. Hoang, Y. Le Bigot, G. Avignon, *Appita Journal*, **2003**, *56*, 102.
- [19] – K. Poppius, J. Sunquist, L. Laamanen, I. Wartiovaara, S. Kauliomäki, *Paperi Ja Puu - Paper and Timber*, **1986**, *2*, 87.
- [20] – J. Gierer, *Wood Sci. Technol.*, **1985**, *19*, 289.
- [21] – L. Kham, M. Delmas, Y. Le Bigot, G. Avignon, *Ind. Crops. Prod.*, **2005**, *21*, 9.
- [22] – J. Gierer, *Holzforschung*, **1990**, *6*, 387.