Acid Extraction of the Alkaline Wood Pulps (Kraft or SODA/AQ) Before or During Bleaching Reason and Opportunity

Alain Maréchal[a]

[a] Laboratoire de Génie des Precédés Papetiers, associé au CNRS n° 1100 Institut National Polytechnique de Grenoble, St Martin d'Héres, Cedex, France

PLEASE SCROLL DOWN FOR ARTICLE

ACID EXTRACTION OF THE ALKALINE WOOD PULPS (KRAFT OR SODA/AQ) BEFORE OR DURING BLEACHING REASON AND OPPORTUNITY

Alain Maréchal
Laboratoire de Génie des Procédés Papetiers, associé au CNRS n°1100
Institut National Polytechnique de Grenoble
Ecole Française de Papeterie et des Industries Graphiques
Domaine Universitaire - B.P.65 - 38402 St Martin d'Hères Cedex - France

ABSTRACT

The decreases in kappa number of an unbleached alkaline hardwood pulp of *carpinus betulus* when performing dilute H_2SO_4 hydrolysis at about 100°C, either after or before oxygen bleaching are the same. The main parameters of this acid hydrolysis are specified by studying the acidification of unbleached alkaline pulp suspensions at room temperature, and the extraction kinetics at temperatures in the range of 88°-110°C by following UV absorbance of the hydrolysis liquors.

Among the dissolved products in the liquors 2-furancarboxylic acid has been identified. This acid results probably from the degradation in the acid medium of compounds present in the unbleached alkaline pulp, which are not oxidized by oxygen in the alkaline medium.

INTRODUCTION

In view of decreasing, or indeed eliminating the production of toxic chlorinated organic materials[1,2] during bleaching with chlorine, various methods are used or are now considered. One approach is the partial replacement of chlorine by chlorine dioxide in the C-stage[3] ; another is to extend the cooking time[4] or to use the "rapid displacement heating" pulping system[5], in order to reduce the chlorine demand of the pulp by lowering the kappa number prior to bleaching.

A more satisfactory solution would be the use of oxygen (or hydrogen peroxide) instead of chlorine; unfortunately the treatment of the pulp with oxygen in the alkaline medium is limited by the existence of a "limit kappa number" beyond which it is not possible to further delignify without degradation of polysaccharides[6]. The numerous investigations carried out to solve this problem do not propose any satisfactory solution, but allowed the industrial development of oxygen bleaching[7] owing to the discovery of a carbohydrate protector[8]: Mg^{2+}. However, the efficiency of magnesium in preserving pulp viscosity occurs only above the "limit kappa number" value[6]. Moreover, the use of this oxygen process only decreases the chlorine demand of the pulp without eliminating the use of chlorine.

We demonstrated[9] in 1979 that pretreatment at 100°C during one hour of the alkaline wood pulp (kraft and soda/AQ) with a dilute sulfuric acid solution (N/65) led to a more thorough oxygen delignification (kappa number~3), without excessive degradation of polysaccharides (viscosity $[\eta]>760$ ml/g). Abrahamsson and Samuelson[10] used a NO_2/O_2-pretreatment of the pulp at 56°C and obtained a smaller but significant improvement in oxygen delignification without excessive degradation of the polysaccharides. Lachenal and de Choudens[11] observed the same improvement with a Cl_2-pretreatment of the pulp at 70°C. Fossum and Marklund[12] reported similar improvements when pretreating the pulp either by ClO_2 at 50°C or by H_2O_2 in an acid medium at 60°C. When pretreating a kraft wood pulp at 70°C by dilute H_2SO_4 (N/22) Gellerstedt and Lindfors[13] obtained a slight decrease in kappa number.

All of these pretreatments are performed in an acid medium at an elevated temperature and we can observe that the bleaching processes of the alkaline wood pulps nowadays make use of a hot acidic stage. The aim of our study is to elucidate the role of the acid medium at about 100°C on an alkaline wood pulp (kraft or soda/AQ) in view of further bleaching by oxygenated compounds.

MATERIALS AND METHODS

Methods of Analysis

Pulp properties were determined according to appropriate standard procedures.

Pulp yield was always determined by weight (o.d.) loss, after pulp washing by running water on a wire mesh (mesh opening: 90 μm) and air drying.

UV absorption: after suitable dilution with distilled water, the absorbance was determined at pH=11 by NaOH addition. The absorbance at 245 nm were calculated for the undiluted liquor on the assumption that the absorbance was directly proportional to the solute concentration.

HPLC used a MERCK "OAHY" column (solvent: H_2SO_4 N/100, flow rate: 0.5ml/min., column temperature: 35°C).

^1H and ^{13}C NMR analysis carried out in "Leningrad S.M.Kirov Forest Technical Academy".

Acidification of the Suspensions

An anhydrous mass, m_i, of air-dried fibers was defiberized with a domestic mixer, with 800g of distilled water (1 distillation, ρ: 0.997g/cm^3, pH: 5.62). Known acid volumes (~1N) were added to the suspension with a microburette at room temperature (~23°C). After each acid addition, the suspension was agitated for two minutes with a magnetic stirrer. The stirring was stopped and the pH was measured with pH-probes dipped directly into the suspension for three to ten minutes until a constant value was obtained.

Kinetic Study of the Hydrolysis Stage (A)

A 20g anhydrous mass of air-dried fibers was defiberized with a known quantity of liquor (about 800ml) in a 1.15 litre stainless steel rotating autoclave, electrically heated. The temperature was increased 3°C per minute. The pH and absorbance measurements were done on successive samples of liquor filtered on a sintered glass crucible (porosity < 5 μm) and frozen.

The buffer solution was made by adding NaOH into a $NaHSO_4$ 0.4M-solution until a measurement of pH ~ 2 was obtained.

Extraction of the Products dissolved by dilute H_2SO_4-Hydrolysis

A 455g anhydrous mass of air-dried soda/AQ pulp of *carpinus betulus* (kappa number: 24.8, viscosity [η]: 930 ml/g) was mixed in 18 litres of distilled water previously acidified with H_2SO_4 up to pH=2. After defiberizing the pulp was

transferred into a twenty-litre stainless steel extractor; the pH of the suspension was equal to 2.18. The suspension was slowly stirred and heated by a water jacket. It took about 40 minutes to reach 95-100°C.

The absorbance at 245 nm of the liquor was 15.0 after two hours at 95-100°C. The hydrolysis was stopped effectively after three hours. After this treatment the yield=96.4%, the kappa number=16.4 and the viscosity $[\eta]$=760 ml/g.

The separated liquor (14.8 litres) was filtered on a sintered glass crucible (porosity<5 μm) and neutralized to pH=7 by adding NaOH and then concentrated to 350 ml by evaporation at 50°C under reduced pressure (water respirator). These 350 ml were H_2SO_4 acidified to pH=1.8 and continuously extracted by chloroform. The chloroform extract was evaporated to dryness at 50°C and analysed.

RESULTS AND DISCUSSION

Influence of Pulp Acid Hydrolysis on further Oxygen Bleaching

We started previously[9] with alkaline (soda/AQ, kraft/AQ and kraft) hardwood pulps of *carpinus betulus* obtained by cooking at 138°C. Those pulps were hydrolysed by dilute sulfuric acid (N/65) before oxygen bleaching. The same method is used but with a cooking temperature of 165°C. The conditions and the results of which are presented in TABLE 1.

Air-dried pulp samples I and II are treated according to, either an acid hydrolysis stage (A) or an oxygen bleaching stage (O), or the two stages in the order of the symbols A and O. A washing with running water on wire mesh is done between each stage. For instance, IOA is for sample I which is first hydrolysed (A), washed, and bleached with the oxygen process (O). The conditions for these treatments are presented in TABLE 2 and the results in TABLE 3.

As compared with a first study[9], we find again the same improvement in delignification(kappa number) without excessive degradation of the polysaccharides (viscosity $[\eta]$>760 ml/g). As shown by de Choudens, Lachenal et al[14], the hot acid washing of the pulp, which eliminates the heavy metal ions, improves hydrogen peroxide delignification. Moreover, they observed that raising the temperature in the acid treatment further decreased the kappa number after the H_2O_2-stage even though the metal ion content of the pulp was not altered. These authors concluded that "a significant amount of ß-ether linkages were left unhydrolysed during kraft pulping

TABLE 1

Soda/AQ-Cooking of air-dried *Carpinus betulus* Wood Chips.

Experiment	I	II
NaOH , g / 100g o.d. wood	20	20
Anthraquinone , g / 100g o.d. wood	0.5	0.5
Liquor-to-wood ratio , l / kg o.d. wood	3.5	3.5
Time to temperature , min.	90	30
Time at 165°C , min.	30	30
Pulp yield , % of o.d. wood	50.1	50.7
Kappa number	20.1	23.1
Viscosity [η], ml/g	888	949

TABLE 2

Conditions for the Oxygen Bleaching Stage (O) and the Hydrolysing Stage (A).

Oxygen Bleaching Stage (O)		Hydrolysing Stage (A)	
NaOH , g / 100g o.d. pulp	3.0	H_2SO_4 , g / 100g o.d. pulp	2.94
Consistency , % in weight	3.85	Consistency , % in weight	2.50
Oxygen , MPa at room temperature	1.0	Time to temperature , min.	15
Total Pressure at 115°C, MPa	1.5	Time at 101°C , min.	60
Protector (Mg^{2+} salt)	none		
Time to temperature , min.	20		
Time at 115°C , min.	60		

TABLE 3

Analysis of Pulps I and II after the Treatments performed in the Order of the Symbols O and A.

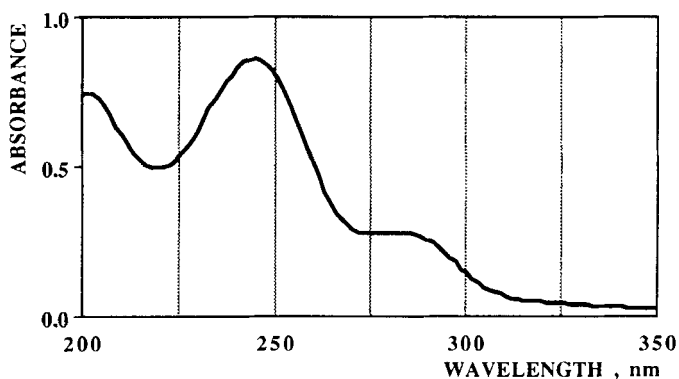| Sequence nature	final pulp yield % o.d. wood	Kappa number	Viscosity [η] ml/g	g furfural / 100g o.d. wood
I	50.1	20.1	888	7.55
I A	47.0	11.7	850	6.72
I A O	44.3	3.2	782	6.30
I O	45.6	9.4	767	6.38
I O A	43.3	2.6	729	6.38
II	50.7	23.1	949	7.52
II A	47.4	15.6	850	–
II A O	44.7	4.2	–	–
II O	46.6	9.8	–	–
II O A	44.1	3.2	–	–

FIGURE 1. UV Spectrum of the hydrolysis Liquors corresponding to Treatment Sequences IA and IOA as quoted in TABLE 3: the two Spectra were identical.

and were cleaved by acidolysing the lignin, consequently formation of carbonyl groups along with release of free phenolic groups was achieved", that favours the dissolution of the lignin during the following H_2O_2-treatment[15].

Our results in TABLE 3 show : –first, the improvement (as measured by kappa number) of the delignification is obtained not only during the oxygen treatment but also during the acid treatment; –second, the kappa number decrease due to the acid treatment alone is about same order whether the hydrolysing stage is done before or after the oxygen treatment (Δ kappa number ~7), so this improvement seems specific to the acid treatment of the pulp.

Therefore, it appears that the third part of the residual oxidizable materials (lignin?) in our pulp obtained after the alkaline cooking, can be dissolved during the acid hydrolysis of the pulp alone, when performed at about 100°C. This assumption is confirmed by UV spectra analysis in the wavelength range 200-350 nm (FIGURE 1) which was done on the hydrolysis liquors : two maxima of absorbance appeared at 245 nm and 285 nm, which are characteristic of a carboxyl group on the side chain of a guaiacyl unit[16,17].

As our measurements of the furfural index (TABLE 3) showed that the hemicelluloses were not significantly dissolved during this hydrolysis stage, as compared to the oxygen treatment alone, i.e. IAO and IOA to IO, consequently we
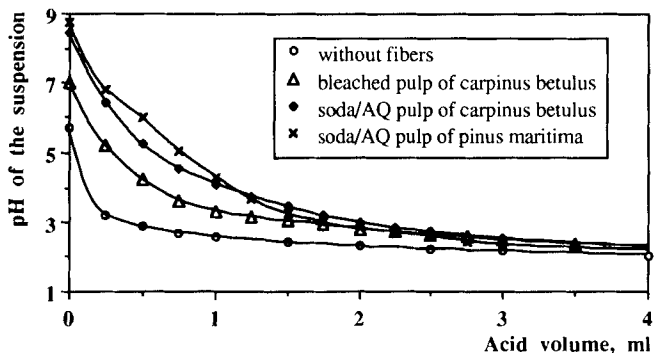
FIGURE 2. Acidification by 1.006N H_2SO_4 at room Temperature of 800g distilled Water containing 10.12g(o.d.) of air-dried Pulp.

were searching for the nature of the dissolved products. In a first step, a kinetic study of acid hydrolysis is necessary in order to know its main parameters.

Study of the Acidification of Alkaline Wood Pulp Suspensions

In principle, the acid hydrolysis of the pulp can be related to the H^+concentration of the suspension , but as the wood fibers behave like cation exchangers[18], the pH of a suspension depends on :

- the quantity of acid introduced,
- the initial anhydrous fiber mass,
- the pulp consistency.

Thus, we have studied the acidification of alkaline wood pulp suspensions according to experimental conditions which are as close as possible to our hydrolysis stage.

For a consistency of 1.25%, we tested four different strong acids : HCl, $HClO_4$, HNO_3, H_2SO_4. We did not observe any difference in behaviour with respect to the anion nature for the pH-range (initial to pH=2) studied.

In the same way, with HNO_3, no differences were observed with soda/AQ *carpinus betulus* pulps at 110, 68, 31.5 and 21 kappa numbers. However, the same experiment performed with a bleached *carpinus betulus* pulp (FIGURE 2)
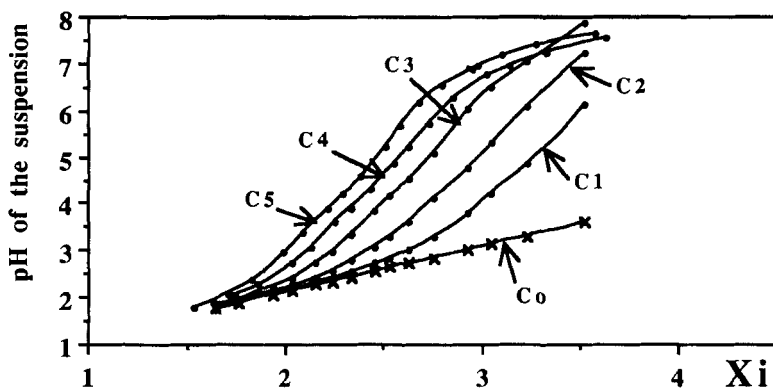
FIGURE 3 . Measured pH of the Suspension of unbleached Soda/AQ *Carpinus betulus* Pulp as a function of Xi, i.e. the Logarithm of the calculated H+Concentration, for several initial Pulp Consistencies: $C_0=0$ (distilled Water); $C_1=0.63\%$; $C_2=1.25\%$; $C_3=2.47\%$; $C_4=3.67\%$; $C_5=4.84\%$.

showed a lesser H+adsorption as compared with unbleached pulp, results which are in agreement with the fact that the last laboratory bleaching stage (CEDED) was done in a buffered suspension (pH=4.8) and that the bleached pulp had a lower total carboxyl value than the unbleached pulp[19].

FIGURE 3 shows the results obtained with 0.944N HNO_3 and several consistencies: we present our measured pH-values as a function of X_i, i.e.the logarithm of the calculated H+concentration.

The electrokinetic properties of the fiber suspensions have been extensively studied[20] and we have chosen to exploit our results according to the model proposed by Grignon and Scallan[21], in which the measured mean water retention value is 1.5 g of water per 1g of anhydrous kraft wood pulp, in a wide range of pH-values.

Assuming that equilibrium is reached between the gel phase (i.e.the solution inside the fiber wall) and the external liquid phase (i.e.the solution outside the fibers), the amount of H+ adsorbed by the fibers is estimated and presented in FIGURE 4.

We observed that the adsorbed H+quantity is a function of consistency and the pH measured and reaches a broad maximum for a constant consistency. Our results
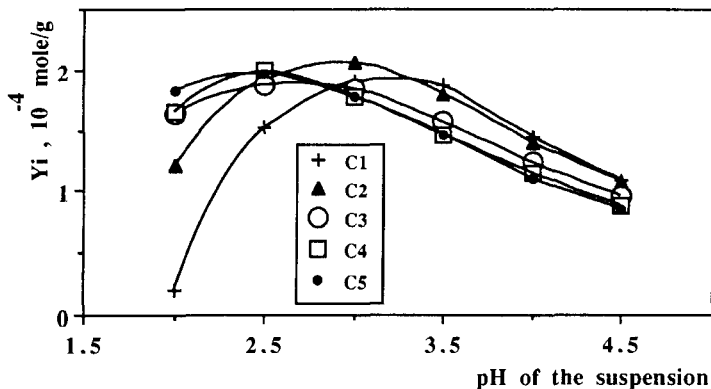
FIGURE 4. Calculated Mole Number of H^+ adsorbed per 1g of anhydrous Fibers, Yi, as a function of the measured pH of the Suspension for several initial Pulp Consistencies: C_1=0.63%; C_2=1.25%; C_3=2.47%; C_4=3.67%; C_5=4.84%.

are in agreement with the model proposed by Grignon and Scallan. The pulp in our experiment was not previously deionized by acid washing and, thus, the increase of the pulp consistency leads to an increase of the salt concentration in the solution. In accordance with the conclusion of these authors, we observed the translation of the H^+ adsorption curves towards lower pH-values when the salt concentration increases. Thus the pH-difference between the solution inside the fibers and the external solution is reduced by an increase in pulp consistency. The curves in FIGURE 4 are only slightly translated along the Y axis for the high consistencies by the value used for the constant water retention value.

Our method is suitable only for pulp consistencies<5% and could be more rigourous by measuring the pH of the external liquid phase before and after separating the fibers by filtration to ascertain that equilibrium was reached between the external liquid and the gel phase. Moreover, the water retention values of our pulp should be determined with respect to the pH.

However, the small water retention value variations registered, by Grignon and Scallan[21] between pH=7 and pH=2 and by Lindström and Carlsson[22] between pH=7 and pH=4, for unbleached kraft wood pulps, added to the fact that our pulp consistency is lower than 5%, make it possible to consider that our approach is

TABLE 4

Hydrolysis of unbleached (kappa number: 20.0; [η]: 979ml/g)Kraft Pulp of *Carpinus betulus*.

Hydrolysing medium	Buffer	Buffer	Buffer	H_2SO_4 (diluted)	H_2O (distilled)
pH of the suspension before hydrolysis	2.10	1.96	1.98	4.13	7.22
Hydrolysis temperature, °C	110	103	88	110	110
Total hydrolysis time, min.	90	150	300	90	235
Total Q, litre	7.80	8.53	7.38	9.56	1.95
Final pH of the suspension	2.09	1.95	1.96	3.73	6.61
Pulp yield, % of o.d. pulp	94.1	96.2	95.8	95.4	93.7
Kappa number	12.1	12.8	13.5	12.2	16.2
Viscosity [η], ml/g	926	972	1024	934	1009

reliable. Taking into account the shape of the curves in FIGURE 4, we believe, as Grignon and Scallan have suggested, that a main parameter of the considered hydrolysis stage (A) is the H^+concentration in the gel phase. The existence of a broad maximum for the adsorbed H^+quantity makes it possible to control the H^+activity, i.e. the H^+concentration in the gel phase for a constant water retention value, either by putting a buffer solution in the suspension, or by acidifying the suspension up to a measured pH in the external liquid phase that is included within the boundary lines of the adsorption plateau.

Kinetic Study of the Hydrolysis Stage (A)

The kinetic study was performed by following the absorbance of the liquor between λ=325 nm and λ=225 nm as a function of hydrolysis time . The results obtained for λ=245 nm are presented in TABLE 4 and on FIGURE 5 where Q, determined by multiplying the absorbance at 245 nm by the volume of the hydrolysis liquor, was corrected with the values obtained for the successive samples of removed liquor.

On FIGURE 5, the Q-values different from zero obtained with H_2O, do not correspond to a maximum of absorbance at 245 nm which was specific to the extracted products when the suspension was acidified before treatment ; in fact, the product(s) of the acid hydrolysis reactions were not extracted by auto-hydrolysis with water in our operating conditions; however, the auto-hydrolysis extracted products had a non zero absorbance value at 245 nm and the conventional
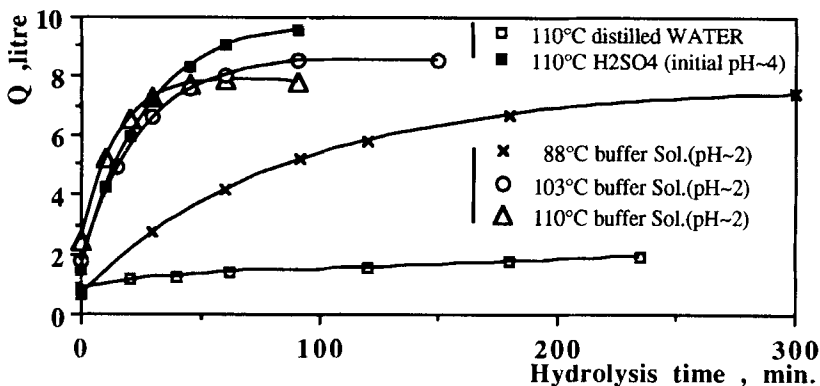
FIGURE 5. Kinetic Study of acid Hydrolysis of unbleached Kraft Pulp of *Carpinus betulus* . Q, is related to the Quantity of extracted Products.

exploitation of these results as kinetics parameters was not possible because we could not assume that the reactions during auto-hydrolysis were independent of the pH-value .

From FIGURE 5, we can determine the initial extraction rates for the three temperatures studied and as a first approximation their relative values would be 1:2:3 at 90°C, 100°C, 110°C respectively.

A second kinetic study at 103°C was performed with the air-dried pulp obtained after the first series of measurements (yield, kappa number, viscosity): the characteristic spectrum, as shown in FIGURE 1, was no longer reproduced; after 135 minutes at 103°C, the absorbance at 245 nm=0.675, the yield of new hydrolysis=96.3%, the kappa number=11.8 and the viscosity $[\eta]$=873 ml/g.This second hydrolysis of an already hydrolysed sample shows that the first extraction was complete and, moreover, we can evaluate the degradation of polysaccharides at 103°C in our operating conditions: $\Delta[\eta]$=0.75ml/g per minute of hydrolysis, this order of magnitude is the same when calculating from results in TABLE 3.

The results from dilute H_2SO_4 hydrolysis at 110°C, with H^+concentration in the external liquid phase 100 times lower (pH~4) than the one used with a buffer solution (pH~2) , but with a theoretical adsorbed H^+quantity per gram of anhydrous fibers equivalent (~1.5 x 10^{-4} mole/g) validate our assumptions to

interpret the acidification of the pulp suspensions and confirm the shape of the curves on FIGURE 4.

Some viscosity values in TABLE 4 are higher than the initial value obtained for the pulp before hydrolysis, these values have been confirmed by new determinations and are not yet explained.

This kinetic study shows nevertheless that the extraction efficiency of the *carpinus betulus* pulp can be obtained in an open reactor at temperatures between 90°C and 100°C. The necessary acid quantity depends on the pulp consistency but, owing to the existence of an adsorption plateau for the H^+ adsorption in the gel phase, in practice, this acid quantity will be added before hydrolysis until the measured pH of the suspension is included in the range 2-3.5 and for a pulp consistency in the range 2.5%-5%. Once these conditions were fixed, we checked the extraction by absorbance measurements in the range λ=325-225nm on samples which were taken from the liquor.

Analysis of the Products dissolved by dilute H_2SO_4 Hydrolysis

After pulp hydrolysis and chloroform extraction of the hydrolysis liquor according to the description in the MATERIALS AND METHODS section, the chloroform extracted material was analysed by ^{1}H NMR (50 MHz, aceton-d6, δ(ppm) : 6.62, 7.22, 7.79, 9.80) and ^{13}C NMR (200 MHz, CDCl$_3$, δ(ppm) : 112.3, 120.0, 144.0, 147.5, 163.4).

This material was mainly 2-furancarboxylic acid (2-FCA), the purity of which can be evaluated by comparison of infrared spectra (A) and (B) in FIGURE 6.

The UV spectrum (FIGURE 7) of the products not extracted by chloroform revealed the absence of a maximum absorbance at λ=245 nm and consequently the 2-FCA was alone responsible for this maximum absorbance[23] in FIGURE 1. At the beginning of this study, this acid had been mistaken for an aromatic compound because of a similar spectrum. The extracted 2-FCA quantity was more than 0.5g per 100 g of anhydrous pulp mass.

Is the 2-FCA responsible for the existence of a "limit kappa number" when performing oxygen bleaching ?

To give a response, a mixture of IO and IIO pulp (TABLE 3) was hydrolysed by dilute sulfuric acid at 110°C and at initial pH of the suspension 2.38. A similar kinetic study as precedingly was performed: after 45 minutes the maximum of
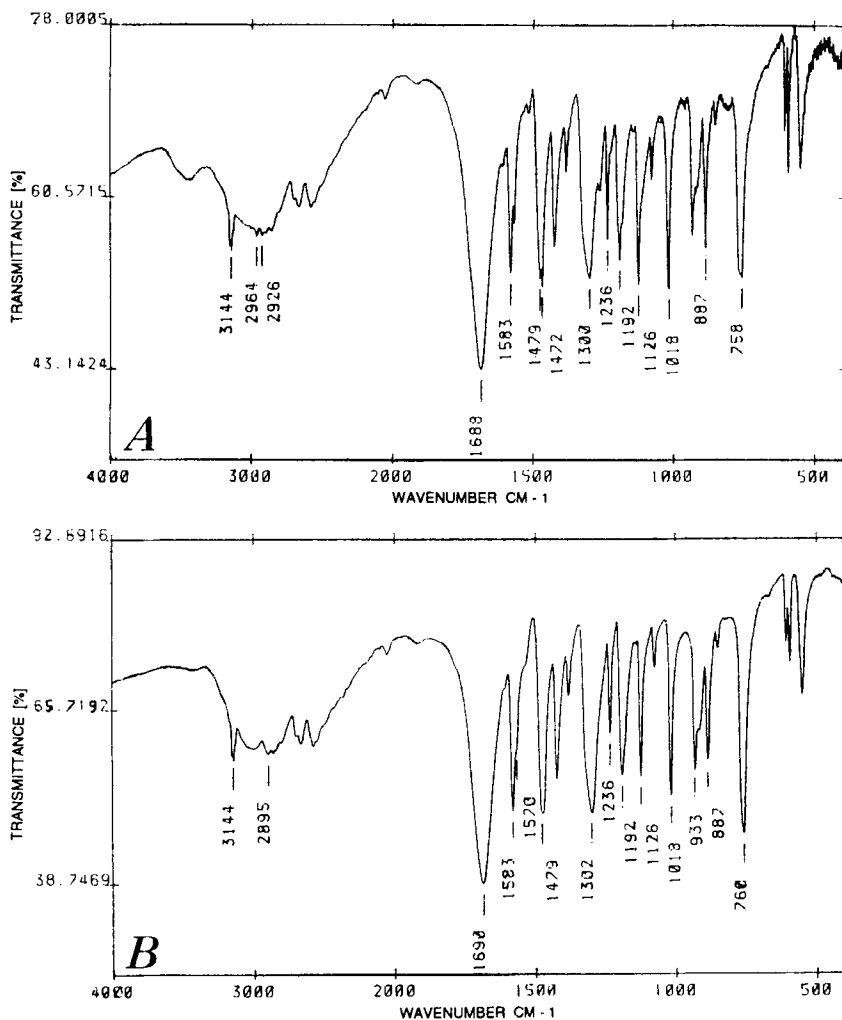
FIGURE 6. Analysis of the dissolved Products during dilute H_2SO_4 Hydrolysis:
(A) : FTIR Spectrum of the Extracted Material by Chloroform.
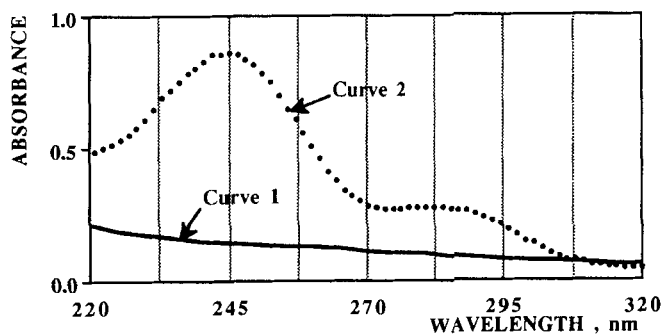(B) : FTIR Spectrum of 2-Furancarboxylic Acid(Purity 98%).

FIGURE 7. Analysis of the dissolved Products during dilute H_2SO_4 Hydrolysis: Curve 1: UV Spectrum of the Remaining Hydrolysis Liquor after Extraction by Chloroform - Curve 2: as in FIGURE 1.

absorbance at 245nm of the liquor became stable: Q=8.54 litres (FIGURE 5).In an independent experiment, when oxidizing the 2-FCA by $KMnO_4$ in the usual conditions of the kappa number measurement, we observed that the kappa number was in correlation with the 2-FCA quantity : gram 2-FCA / 100g(o.d.) pulp = 0.23.kappa number.

These results and those in TABLE 3 show the relation which exists between the kappa number reduction and the appearance of 2-FCA in the acid hydrolysis liquors. The "limit kappa number" observed in the oxygen bleaching would be due to the presence in the unbleached *carpinus betulus* pulp of materials which can release 2-FCA in acid medium and which are not oxidized during oxygen bleaching.

The treatment in acid medium of alkaline wood pulps is known to decrease the physical properties of the manufactured papers, essentially the tear index. To evaluate the impact of the acid extraction in this work we refined our original 455g of pulp which had been extracted by hydrolysis in a valley beater. The physical characteristics are presented in TABLE 5 and can be compared with both those from the same soda/AQ pulp of *carpinus betulus* , but after bleaching, and those from a bleached kraft pulp of *carpinus betulus*. (The bleaching process in the two cases was a classical laboratory bleaching CEDED).

TABLE 5

Properties of chemical Wood Pulps of *Carpinus betulus* after Refining in a Valley Beater.

A : Soda/AQ Pulp hydrolysed with dilute H_2SO_4 (original 455g).
B : Soda/AQ Pulp bleached with classical Laboratory CEDED-Sequence.
C : Kraft Pulp bleached with classical Laboratory CEDED-Sequence.

Pulp Type	A	A	A	B	B	C	C
(*) Rifining Time,min.	0	18	19	0	63	0	58
Shopper-Riegler Freeness,°SR	21	60	72	15	68	18	65
Water Retention Value, g/g.100	137	178	229	116	202	112	207
Bauer-McNett classification,wt.%							
35-mesh	60.8	59.7	47.4	49.4	26.1	47.5	27.0
65-mesh	21.2	16.5	24.0	28.1	21.6	33.5	20.0
100-mesh	5.3	5.8	5.7	5.7	12.0	7.0	17.5
150-mesh	2.3	3.8	4.1	1.4	7.2	2.0	10.0
passed 150-mesh	10.4	14.2	18.8	15.4	33.1	10.0	25.5
Bulk, cm3/g	1.23	1.22	0.98	1.90	1.24	1.95	1.36
Zero-span tensile, LRo(wet), m	9100	7900	5600	12150	9500	10050	9350
Zero-span tensile, LRo(dry), m	12300	13300	12600	12680	14700	11870	13900
Breaking length, LR, m	3700	7500	7600	2170	8260	2000	6950
(LR/LRo(dry)).100	30.0	56.4	60.0	17.1	56.2	16.8	50.0
Burst index, kPa.m2/g	2.40	4.50	4.10	1.23	4.35	1.79	4.92
Tear index, mN.m2/g	4.90	5.10	4.60	10.24	10.15	9.30	7.93
Double fold (450g), number	--	--	--	8	3230	52	3355
Double fold (700g), number	21	320	570	--	--	--	--

(*) The refining time corresponds to the application time of the movable weight on the bedplate lever arm of the valley beater which goes on when the movable weight is removed .

The first remark deals with the high refining rate of the hydrolysed pulp: 18 minutes are necessary to obtain °SR: 25 for the reference kraft or soda/AQ pulps, which explains our lack of measurements between °SR: 21 and °SR: 60.

The Bauer-McNett classification, show a cut of the fibers much less significant than for the reference pulps, higher values of the WRV and of the ratio LR/LRo, overall evidence of the highest hydration capacity for the hydrolysed pulp and consequently a better aptitude for refining; however, the two conclusions should be certified by appropriate microscopic studies of the pulp during refining.

As expected the tear index was largely decreased, the burst index and the breaking length were the same, meanwhile the double fold was clearly improved: it was necessary to increase the weight of the load from 450g to 700g to obtain the break of the test piece before excessive duration.

As the hydrolysis parameters were chosen to study conveniently the nature of the dissolved products, the measured physical characteristics were probably not the best; in fact, taking into account the kinetic study results, we can suppose that an
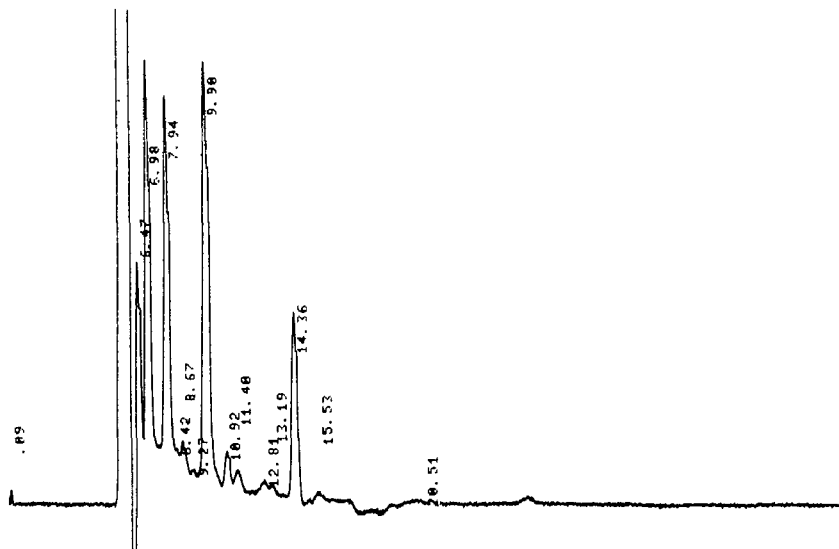
FIGURE 8. Analysis of the dissolved Products during dilute H_2SO_4 Hydrolysis: HPLC Chromatogram (organic Acids) of the Remaining Hydrolysis Liquor after Extraction by Chloroform

acid extraction performed at about 100-110°C during less than one hour, which would give the same chemical results, would preserve the tear index, as well as maintain the same refining aptitude and increase the double fold.

Prospects

Does the 2-FCA come from the H^+ catalysed degradation of product(s) that cannot be oxidized by oxygen in the alkaline medium ?

For this purpose, we separated the extracted acids by HPLC from the hydrolysis liquors that were obtained after the acid hydrolysis stage (A) performed before the oxygen bleaching stage (O) (FIGURE 8) and after it (FIGURE 9). The acids characterized by retention times of 26 minutes and 35 minutes are missing on FIGURE 8 since this liquor had been extracted by chloroform in the first part of this study.
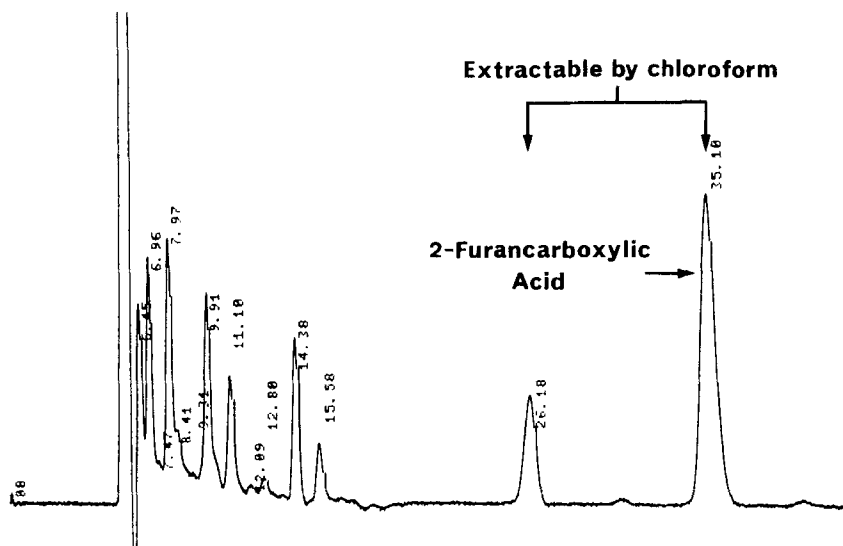
FIGURE 9. Analysis of the dissolved Products during dilute H_2SO_4 Hydrolysis performed after Oxygen Bleaching: HPLC Chromatogram (organic Acids) of the Hydrolysis Liquor.

The same experiment (HPLC) was done with the mixture of two liquors (FIGURE 10) and we observed the same five acids (their identifications are in progress in our laboratory) for the two liquors (their retention times being: 6'47", 6'97", 7'94", 9'91", 14'38"). The presence of identical degradation products and a similar kappa number reduction (Δ kappa number~7) for the two corresponding pulps, mean that 2-FCA arises from degradation of the same compounds which are present in the unbleached alkaline pulp[24] and which are not oxidized by oxygen in alkaline medium.

Does this compounds also exist in the softwood pulps?

For this purpose, we hydrolysed a soda/AQ pulp of *pinus maritima* (kappa number: 30.1) in a buffered suspension (pH: 1.95) at 103°C. We found the same UV absorption spectrum as in FIGURE 1, but yet the extracted quantity (Q on FIGURE 5) after 2.5 hours is three times less important than for *carpinus betulus* : effectively, the relative initial rate of extraction, as defined previously, was equal to
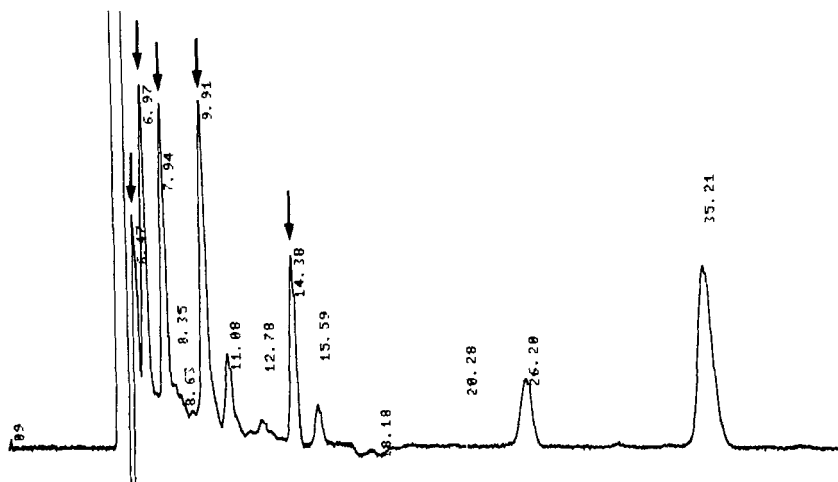
FIGURE 10. HPLC Chromatogram (organic Acids) of the Mixture of the two Liquors corresponding to FIGURE 8 and FIGURE 9.

1 for *pinus maritima* against 2.3 for *carpinus betulus*. This gap may be explained by the difference in their behaviours when performing the acidification of the unbleached pulps (FIGURE 2), therefore, it could be recommended to perform the acid extraction of *pinus maritima* at higher pH than 1.95.

Nevertheless, the existence of the characteristic UV spectrum (FIGURE 1) tends to prove the presence in the softwood pulps of materials which can release 2-FCA in acid medium, that could explain, the efficiency of a ripening at 90°C during 3 hours carried out after the treatment of an unbleached *pinus sylvestris* pulp by nitrogen oxides[25], and of the x stage in the EO x EO process[26].

CONCLUSIONS

The presence, in the unbleached hardwood pulps of *carpinus betulus* issued from alkaline cooking (kraft or soda/AQ), of compounds that are not oxidized by oxygen in the alkaline medium, can explain the existence in the oxygen bleaching

process of a "limit kappa number" beyond which the polysaccharides are still degraded and the delignification (as measured by the kappa number) can no longer be improved.

This compound(s) can be degraded and dissolved in the acid medium to release, among other materials, 2-furancarboxylic acid; a quantity of this acid greater than 0.5g per 100g of o.d.pulp was obtained by chloroform extraction of the hydrolysis liquor.

The main parameter that governs the dissolution of this compound(s) in the acid medium is the quantity of adsorbed H^+ per gram of o.d.pulp (i.e. the H^+concentration in the water inside the fibers) which, in the case of *carpinus betulus,* presents a maximum adsorption which looks like a plateau. For a fixed H^+activity (measured by the pH in the external solution) the H^+concentration difference between the solution inside the fibers and the external solution is decreased by increasing the pulp consistency, i.e.increasing the ionic strength of the external solution. Thus, in our case, the acid extraction is more efficient when the measured pH of the suspension is in the range of 2-3.5, and for pulp consistency in the range of 2.5%-5%.

A test with an alkaline pulp of *pinus maritima* showed that the pH range depends on the nature of the pulp.

Another important parameter is the acid extraction temperature, total extraction can be achieved in the 90°C-110°C range; the initial relative rates of extraction vary linearly in the ratio of 1:3 between 90°C and 110°C.

Our complete extraction at 103°C during 90 minutes, which involves a viscosity decrease evaluated at only $\Delta[\eta]=65$ml/g, shows that it is possible to optimize an acid pretreatment of the alkaline pulps in view of a free chlorine bleaching process and, perhaps without toxic organic materials.

REFERENCES

1. D.W. Reeve and P.F. Earl, CPPA Annual Mtg 75 Preprints, Vol. B, p.147-152, CPPA, Montréal, 1989.

2. N.Mc Cubbin, J.B.Sprague and N.Bonsor, CPPA Annual Mtg 75 Preprints, Vol. A, p.393-400, CPPA, Montréal, 1989.

3. R.M.Berry, R.H.Voss, P.E.Wrist, B.I.Fleming, C.E.Luthe, CPPA Annual Mtg 75 Preprints, Vol. B, p.349-350, CPPA, Montréal, 1989.

4. S.A.Heimburger, D.S.Blevins, J.H.Bostwick and G.P.Donnini, Tappi 71 (10), 51 (1988).

5. E.K.Andrews, Tappi 72 (11), 55 (1989).

6. A.Maréchal and A.Robert, ATIP rev. 35 (8), 415 (1981).

7. L.Tench and S.Harper, Tappi 70 (11), 55 (1987).

8. A.Robert , P.Traynard and O. Martin-Borret, French Pat. 1,387,853 (1963).

9. A.Maréchal and A.Robert, Hardwood Pulps in Papermaking, Finnish Pulp and Paper Research Institute Preprints, Finnish-French Symposium October 9-10, Helsinki, 1979.

10. K.Abrahamsson and O.Samuelson, Sven. Papperstidn. 85 (3), R27 (1982).

11. D.Lachenal and C.De Choudens, Cellulose Chem. Technol. 20, 553 (1986).

12. G.Fossum and A.Marklund, Tappi 71 (11), 79 (1988).

13. G.Gellerstedt and E.L.Lindfors, Tappi 70 (6), 119 (1987).

14. D.Lachenal, C.De Choudens, L.Soria and P.Monzie, TAPPI International Pulp Bleaching Conf. May 24-26, p.145, Portland (1982).

15. H.M Chang and G.G.Allan, Lignin: Occurrence. Formation. Structure and Reactions, p.450, K.V.Sarkanen and C.H.Ludwig (eds), Wiley Interscience, New-York, 1971.

16. J.Polcin and W.H.Rapson, Pulp Paper Mag.Can., december 19, 99 (1969).

17. J.Bayer, <u>Absorption Spectra in the Ultraviolet and Visible Region</u>, Vol.XVI, p.143-144, L.Làng (eds), Akademiai Kiado Budapest, 1972.

18. E.Sjöström, Nordic Pulp Pap. Res.J., 2, 90 (1989).

19. R.S.Ampulski, Nordic Pulp Pap.Res.J., 1, 38 (1989).

20. G.Sarret, <u>Contribution à l'Etude des Propriétés Electrocinétiques des Suspensions Fibreuses</u>, p.5-36, Thèse Doct.Ing.Faculté Sciences Université Grenoble, Grenoble, 1967.

21. J.Grignon and A.M.Scallan, J.Appl.Polym.Sci., 25, 2829 (1980).

22. T.Lindström and G.Carlsson, Sven.Papperstidn., 85 (3), R14 (1982).

23. M.Sòti and F.Sòti, <u>Absorption Spectra in the Ultraviolet and Visible Region</u>, Vol.XX, p.247-248, Akademiai Kiado Budapest, 1975.

24. M.R.S.Clemente, K.V.Sarkanen and S.E.Sundin, Sven.Papperstidn, 84 (3), R1 (1981).

25. P.Larsson and O.Samuelson, J.Wood Chem.Technol., 10 (3), 311 (1990).

26. D.Lachenal and M.Muguet, CPPA Annual Mtg 75 Preprints, Vol.B, p.187-192, CPPA, Montréal, 1989.