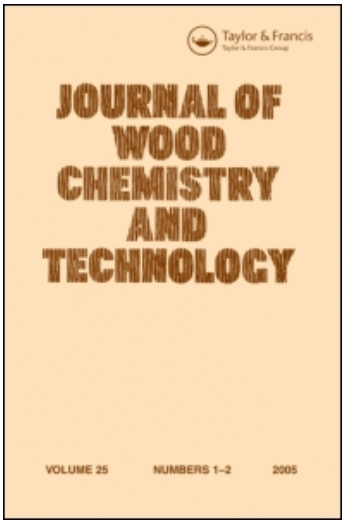

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QUATAM PROCESS—NEW SULFUR-FREE DELIGNIFICATION

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ABSTRACT

An essentially new alkaline chemical pulping process—the Quatam process—has been introduced using an organic base for producing cellulose fibers from wood and annual plants. Solutions of quaternary ammonium compounds, preferably tetramethylammonium hydroxide (TMAH), serve as pulping liquors. The process produces high quality pulp with low kappa number, high brightness and good viscosity—without using sulfur-containing compounds. The process is suitable for both hardwood and softwood. The pulping selectivity of TMAH is demonstrated. Bleachability and mechanical properties of the resulting pulp are compared to those of conventional Kraft pulp.

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INTRODUCTION

In the last two decades efficient chemical recovery systems and nearly closed or practically closed pulping technologies have been developed for Kraft and sulfite pulping in order to make them environmentally friendlier. Nevertheless, there has been great interest in developing radically different methods to reduce or to avoid the use of sulfur compounds while preserving or even increasing the quality of the cellulose fiber produced, to improve the selectivity of delignification, to reduce potential for air and water pollution associated with pulping and bleaching, to minimize water consumption, and to favor subsequent chemical utilization of the isolated lignin.

Of the alternative processes which do not use sulfur in the cooking liquor the organosolv processes based on the solubility of lignin in organic solvents have attracted the most attention and have even been implemented in pilot plant productions. Besides methanol and ethanol which were suggested for delignification already in 1931,[1] numerous organic solvents have been tried and evaluated as pulping liquors including other alcohols, ethers, esters, organic acids, ketones, phenols, dioxane, etc., but none of these can dissolve lignin from wood without the lignin having been broken down to some extent beforehand.[2–4] In the Alcell process[5] a mixture of ethanol and water is used and the acetic acid released from the wood makes the process suitable for hardwood. For pulping of softwoods the addition of catalysts such as mineral acids, Lewis acids, or magnesium chloride is necessary. If organic acids, especially acetic acid, are used as a solvent in the pulping process there is no need for additional chemicals (Acetosolve process). A combination of acetic and formic acid or acetic acid and ethylacetate (ester pulping)[6,7] has some advantages but the process in that case is more complicated. Formic acid even with the addition of hydrogen peroxide (Natural pulping) is suitable only for delignification of straw, nevertheless, the process is very environmentally friendly.[8]

Breakdown of lignin before dissolving it, can be effectively promoted not only by acids but also by alkali. Addition of sodium hydroxide and a catalytic amount of anthraquinone was suggested in the Organocell process.[9,10] The quality of the pulp was, however, unsatisfactory.

The solvents have attracted great interest also as reinforcements in existing pulping processes. Addition of methanol increases the removal of lignin and improves the delignification selectivity. Soda pulping with 40% methanol in the pulping liquor was suggested as a potential sulfur-free alkaline pulping method in Japan (soda-methanol pulping).[11] The Organocell process can be considered as a methanol reinforced soda-antraquinone pulping.[12] Addition of methanol was found to be advantageous in the Kraft and alkaline sulfite processes (methanol-Kraft and ASAM pulping[13,14]),

but the recovery of chemicals from the multicomponent pulping liquor is more difficult.

Despite extensive efforts, neither the organosolv nor the solvent-reinforced processes have found real application. The advantages gained by the solvents do not compensate for the technological difficulties, often problems with the quality of the pulp as well as the high cost of methanol or ethanol recovery.

Modified versions of the conventional Kraft, sulfite, and soda processes using small or catalytic amounts of additives which do not disturb the recycling process and produce better quality pulp have shown more promise of gaining wider application. The most widely tried and used additives are the anthraquinone (AQ) and related compounds which increase both the rate of delignification and the selectivity of pulping, making the carbohydrates more stable toward alkaline degradation. Addition of AQ was reported for the first time in 1977 in soda-AQ pulping.[15]

In recent years the application of surfactant-based additives has injected novelty into pulping technology. Nonionic surfactants are added to the pulping liquor to increase its wetting and penetration properties.[16,17] The surfactants as additives have been shown to be effective in reducing of the kappa numbers, aiding deresination, and producing more uniform pulps. Compared to anionic and cationic surfactants, nonionics were found to be the most effective. The bleachability is not affected.[18]

Another area of non-sulfur pulping is delignification with ammonia or various primary, secondary and tertiary amines in aqueous solutions or in the gaseous phase.[19–21] Liquid ammonia is able to open hydrogen bonds. Although it can soften wood it does not dissolve lignin. Dilute aqueous ammonia solutions can digest straw and undepithed bagasse.[22] Among amines the effect of ethanol amine has been the mostly investigated. Relatively good results were achieved using primary amines.[23] Comparing the activity of primary, secondary and tertiary amines in soda-pulping, methylamine had the greatest effect and trimethylamine the least.[24] Kubes et al.[25] investigated the effect of 23 amino compounds in wood pulping. The authors concluded that amines alone cannot delignify wood but when added to soda liquor they accelerate the delignification. The one exception was 1,6-hexamethylene diamine which by itself was able to extract lignin from both hardwood and softwood but the pulp in both cases was difficult to bleach. When using ammonia or amines for delignification the possibility of condensation with carbohydrates and lignin must be taken into account. Amines or aqueous amine solutions were also tried in supercritical delignification some years ago.[24,26,27] All these alternative sulfur-free processes have shortcomings. To date, they have not been applied on any real scale.

The aim of our paper is to present an essentially new sulfur-free chemical pulping process using an organic base, tetramethylammonium hydroxide (TMAH), in the pulping liquor, as a single reagent. The effect of TMAH in delignification processes has never been previously studied. It has recently been used in pyrolysis-GC/MS analysis of polymers and, in larger quantities, in the electronic industry for cleaning of semiconductor surfaces. In this paper we characterize the new pulping chemical and demonstrate its effectiveness in the pulping of hardwood and softwood species. The advantages and disadvantages of this process, compared to conventional pulping processes are also presented.

RESULTS AND DISCUSSION

In alkaline pulping processes the base used is almost exclusively sodium hydroxide. In the present work instead of NaOH, an organic base—tetramethylammonium hydroxide (TMAH, Fig. 1), a quaternary ammonium hydroxide—was used as pulping chemical.[28] This novel pulping process using TMAH will be referred to below as the "Quatam process".

For preparative purposes TMAH is available in solid form (white crystals) with 5 mol crystal water (approx. 50%). It has a melting point of 65–68°C; and a self-ignition point of 469°C. It is commercially available for technical use as an aqueous solution (approx. 2.8 mol/L). The aqueous solution is clear, slightly yellow with a density similar to water. Other characteristics of TMAH are summarized in Table 1.

Aqueous TMAH solutions proved to be very effective delignification agents. Table 2. shows examples for hardwood and softwood pulping. The quality of the pulp produced and efficiency of the process were assessed through kappa-number, viscosity, brightness, and yield.

The pulps had very low kappa-numbers, satisfactorily high viscosities, and excellent brightness. The fibers were long, soft, and very light. The yields paralleled the low kappa numbers and were comparable to yields of chemical pulps. It must be emphasized that these experiments were carried

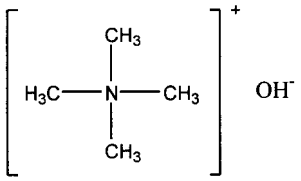

Figure 1. Tetramethylammonium hydroxide.

Table 1. Some Characteristics of Tetramethylammonium Hydroxide (TMAH)

Specification	Molecular weight: 91.2 g/mol Color: very light yellow Density: 1.01 kg/L Explosion levels in air: lower level—36% upper level—6.7% incompatible with aluminum, zinc and (yellow) brass
Stability	Above 134°C decomposes into trimethylamine and methanol
Specialties	Light alkylating agent, Catalyst in some reactions, Fungicidal and bactericidal effect
Application	Development agent for photo resists, Cleaning agent for semiconductors

Table 2. Pulping Parameters and Pulp Characteristics

Wood	Reactor	TMAH (mol/L)	T (°C)	t (min)	W : L	κ	$[\eta]$	Brightness (%)	Yield (%)
Beech wood	R50	1.4	170	60	1 : 5	10.8	844	42.5	43.2
	R1000	0.3	170	100	1 : 35	18	1044	41.8	45.1
Scotch pine	R100	1.7	173	75	1 : 5.5	17.5	910	41.2	39.0
	R100	1.2	186	60	1 : 5.3	22	714	40.6	41.0

out in laboratory batch reactors without optimizing the process or process technology, and without even circulating the pulping liquor. This means that aqueous TMAH solutions can be used for delignification of both hardwood and softwood species.

TMAH has never before been used as a pulping agent. The lack of attention it has received is perhaps due to its relatively low decomposition temperature compared to conventional pulping temperatures. As shown in Table 1, TMAH decomposes on heating at the low temperature of 134°C into trimethylamine and methanol. It can be supposed that the observed high pulping effect at about 170°C is not due to the TMAH itself but also to the degradation products, i.e., trimethylamine and methanol. Indeed, both of these were used in alternative pulping processes. However, according to Kubes et al.,[29] although trimethylamine increases the rate of soda pulping but it does so to a lesser extent than other amines do. Despite a high concentration—40% on o.d. wood—the effect remained far behind the

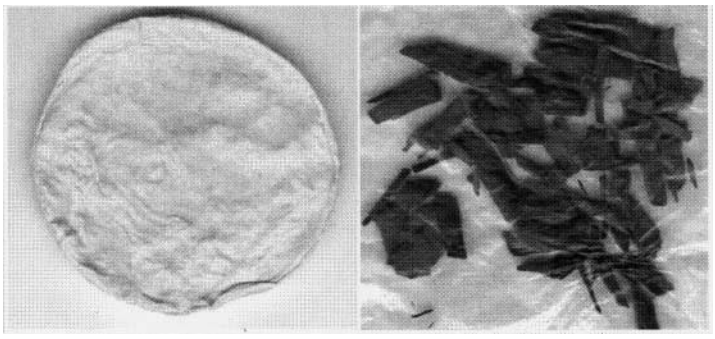

Figure 2. Pulping effect of TMAH, trimethylamine, and methanol.

rate of Kraft pulping. The pulping effect of an aqueous TMAH solution and that of an aqueous mixture of trimethylamine and methanol, in a concentration corresponding to that of TMAH when cooking softwood under the same conditions, are compared in Fig. 2. There is a clear contrast between the two sets of results.

While very effective pulping was achieved with TMAH, the methanol-trimethylamine mixture did not liberate the cellulose fibers from the wood structure and dark brown colored chips were produced. Clearly, therefore, the good pulping result in Table 2 are due to the TMAH and not to its decomposition products. We controlled the decomposition of TMAH. In a closed system the pressure that develops during the cook (6–10 bar) is enough to restrict the decomposition of TMAH. Across a broad range of pulping conditions the rate of decomposition of TMAH does not exceed 2–8% depending on the temperature and cooking time.

Choosing higher analogues of quaternary ammonium hydroxides results in less pulping effectiveness. In a previous paper,[30] we compared the effect of a number of quaternary ammonium hydroxides as pulping chemicals in the delignification of scotch pine and beech wood, including tetramethylammonium hydroxide, tetraethylammonium and tetrabutylammonium hydroxide, as well as benzyltrimethylammonium hydroxide. Using, for example, tetraethylammonium hydroxide to pulp beech wood resulted in a pulp which had lower brightness and significantly higher (about 60%) kappa number compared to TMAH pulping under the same conditions. Increasing the mol mass of the quaternary ammonium base decreases the pulp yield, because of the higher solubility of the cellulose. The higher the molecular mass of the quaternary ammonium hydroxide the better its swelling effect, and above a given concentration it can dissolve cellulose.[31–33] Tetraethylammonium hydroxide above 2.8–3.0 molar

concentration dissolves cellulose, while aqueous solutions of benzyltrimethylammonium hydroxide dissolves cellulose at 1.5–1.8 molar concentrations at room temperature.[34] TMAH does not dissolve cellulose.

It may be concluded, therefore, that TMAH is the best quaternary ammonium hydroxide for wood pulping among the quaternary ammonium hydroxides studied. Tetramethylammonium hydroxide is a strong base similar to the alkali metal hydroxides. As a pulping chemical, there are, however, some very important differences, that distinguish TMAH from the alkali hydroxides. It is well known that the effect of a base depends not only on the concentration of the hydroxyl ions, but also on the type of counter cation (as mentioned above, for example, in connection with the solvent ability of various quaternary ammonium hydroxides.) In a study of the effects of aqueous solutions of ammonium and sodium hydroxides on pulping, the pH difference between the interior of the chips and the pulping medium was observed to be influenced by the cation-type.[35] This difference — among others — must be more enhanced in the case of TMAH, where the cation is not only bigger in size, but has some lypophylic tendencies, due to the methyl substituents of the nitrogen. In another comparison of NaOH with TMAH[36,37] the higher efficiency of TMAH is discussed.

Physical Properties of Quatam Pulp

In order to obtain enough pulp to determine its physical properties, large scale experiments with Scotch pine were carried out in an 18-L reactor. Cooking conditions and pulp characteristics are shown in Table 3. The yield of Quatam pulp was significantly lower, but the cooking was carried out without optimization in contrast to the best optimized Enerbatch Kraft pulp.

For the purpose of measuring physical properties, Quatam pulp with kappa number 16.3 was chosen and compared to a Kraft pulp having a similar kappa number and viscosity (see Table 3).

Table 3. Cooking Conditions and Pulp Characteristics

Wood	Sample	TMAH (mol/L)	T (°C)	t (min)	W : L	κ	$[\eta]$	Brightness (%)	Yield (%)
Scotch pine	Quatam1	1.7	170	60	1 : 4.7	26.8	960	36.6	42.8
	Quatam2	1.6	170	90	1 : 5	16.3	865	45.4	41.3
Scotch pine	Kraft-pulp	–(*)	170	89		15.6	873	51.5	44

(*) EA: 28% as NaOH; Sulfidity: 30% (Enerbatch process).

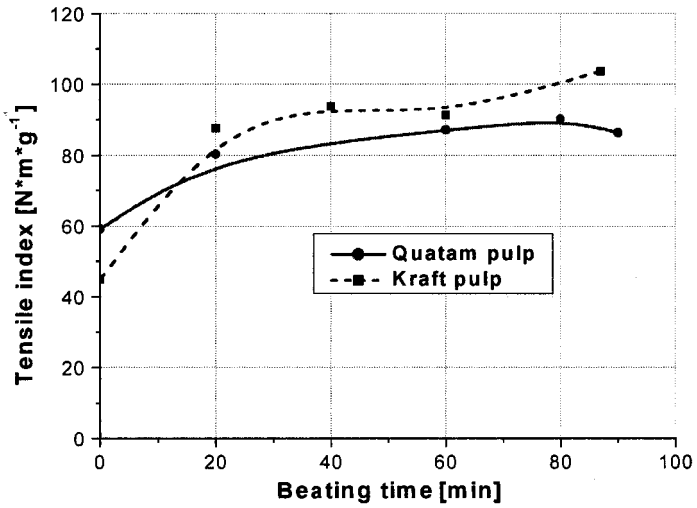

Figure 3. Tensile index of unbleached Quatam and Kraft pulp.

The tensile and tear indices were measured as a function of beating time. The tensile index was somewhat less than, but similar to that of the Kraft pulp (Fig. 3). The Quatam pulp exhibited, however, a much higher tear index than the Kraft pulp (Fig. 4). Although quaternary ammonium hydroxide is not an amine, this behavior of the tear index is reminiscent of the results of Kubes et al.[29] for amine pulping higher tear indices were observed for soda-amine pulps (especially with an ethylenediamine additive) and somewhat lower breaking length and burst strength compared to Kraft pulps.

The Quatam fiber differs somewhat in appearance from Kraft pulp fiber as can be seen in the electron micrographs in Fig. 5.

The alkali resistance of Quatam fibers is very good. The R_{10} and R_{18} values are between 90 and 95, respectively, clearly higher than those of the reference Kraft pulp. The R_{10} and R_{18} values of unbleached Quatam and Kraft pulps are shown in Table 4.

BLEACHABILITY IN TCF-BLEACHING

The bleachability of Quatam pulp in a five stage TCF bleaching sequence was compared with that of Kraft pulp. The bleaching conditions are presented in the experimental section.

The characteristics of the bleached pulps are shown in Table 5. TCF bleaching resulted in higher brightness for Quatam pulp than for the

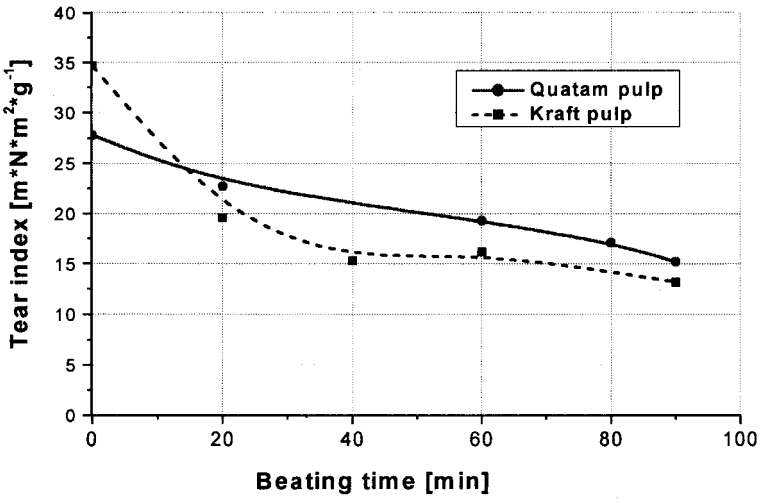

Figure 4. Tear index of unbleached Quatam and Kraft pulp.

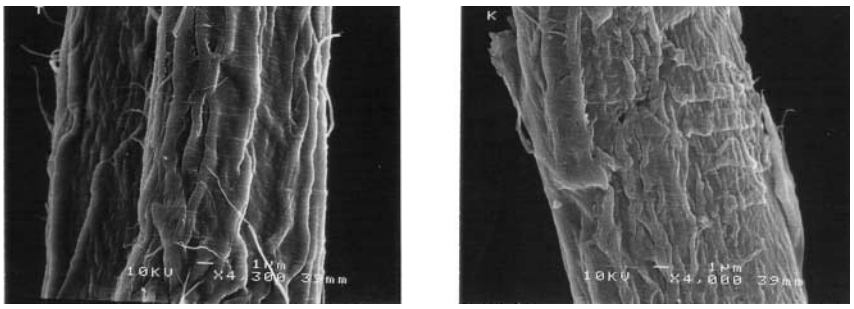

Figure 5. SEM picture of Quatam and Kraft pulp.

Table 4. Alkali Resistance of Quatam and Kraft Pulp from Various Wood Types

		R_{10} (%)	R_{18} (%)
Scotch pine	Quatam pulp	91.6	94.3
Beech wood	Quatam pulp	92.6	94.5
Spruce pine	Quatam pulp	91.2	94.1
	Kraft pulp	89.9	91.5

Table 5. Characteristics of the Bleached Pulps and the Bleaching Process

	Unit	Quatam Pulp	Kraft pulp
Brightness	% ISO	91.5	90.6
Viscosity	mL/g	537	544
H_2O_2 uptake (in P)	from 1%	0.74	0.88
H_2O_2 uptake (in EOP)	from 2%	1.72	1.82
O_3 uptake (in Z_Q)	%	0.41	0.47
Mg (after Q stage)	mg/kg	13	24
Ca	mg/kg	140	270
Mn	mg/kg	0.3	0.9
Fe	mg/kg	6.0	9.9
Cu	mg/kg	<1	<1

reference Kraft pulp at the same viscosity values. In the bleaching process the Quatam pulp consumed less peroxide and ozone than the Kraft pulp. The lower reagent consumption means that chemical and energy costs can be reduced. The fact that Quatam pulp is easier to bleach opens up the possibility that pulping may be terminated at higher kappa numbers, thus saving time and increasing the yield. After the Q stage Quatam pulp contains less heavy metal ions, which is advantageous in view of yellowing of the fibers.

The tensile index and tear index were determined also after the bleaching. The differences in mechanical properties between the Quatam and Kraft pulps became less noticeable. Both the tensile index and the tear index of the two fibers became more similar after bleaching as shown in Figs. 6 and 7.

CONCLUSIONS

We have succeeded in developing a new sulfur-free chemical pulping process, the Quatam process, which uses tetramethylammonium hydroxide as pulping agent and produces high quality dissolving pulps. The main advantages of the new process are: it does not use sulfur-containing compounds, only a single chemical is required, the utilization of lignin from the black liquor is not restricted by sulfur content, the cooking time can be shortened while a high quality pulp is produced. There is no danger of deposition of lignin. The kappa numbers of the Quatam pulp are as low as those of the best Kraft pulps. The pulp is light in color and easy to bleach.

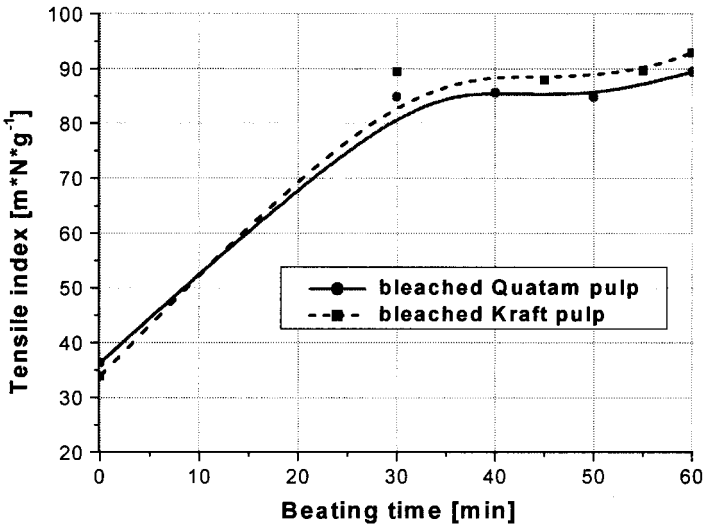

Figure 6. Tensile index of bleached Quatam and Kraft pulp.

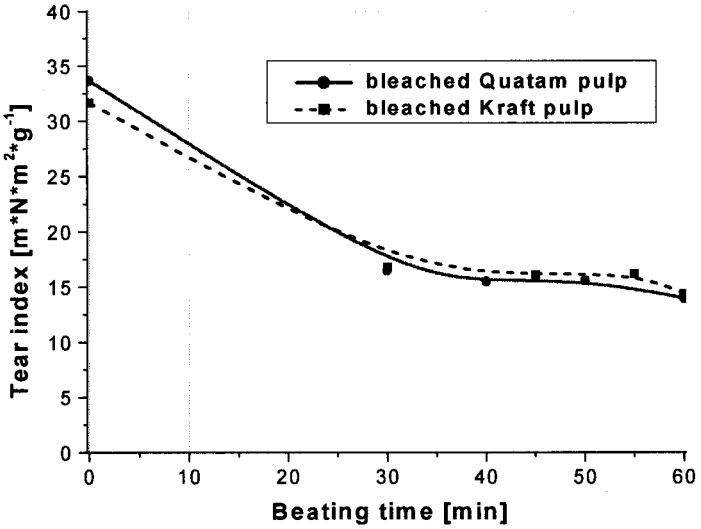

Figure 7. Tear index of bleached Quatam and Kraft pulp.

In a bleaching sequence a higher brightness can be achieved with lower chemical usage. The process is efficient for both hardwood and softwood.

Because TMAH is more expensive than the sodium hydroxide and because Quatam pulp's alkali resistance values are very good, the Quatam process may be recommended first of all in the production of specialty or dissolving pulps. Although it is doubtful that in the near future the Quatam process will unseat the Kraft process it may find a market niche of its own within the industry. Above and beyond the concrete experimental results, utilization of the new chemical, alone or in various processes, can open up new vistas. With an eye towards future industrial application, the Quatam process ought to be implemented with technology for recycling of TMAH. One possible method to recycle the TMAH from the black liquor would be through membrane electrodialysis. Blanco and his colleagues[38] successfully applied this technology to retrieving NaOH from black liquor of straw pulping.

Experimental work is continuing on the process.

EXPERIMENTAL

Materials

Tetramethylammonium hydroxide in a 25% aqueous solution was supplied by CFZ Zaltbommel.

Beech wood was chipped at Lenzing AG to an average thickness of 4.0 mm, an average length of 20 mm, and an average width of 10 mm. Scotch pine (Pinus Sylvestris) and spruce pine, chipped similarly, was provided by Impco-Voest-Alpine and Zellstoff Pöls AG, respectively.

Pulping and Bleaching

Most of the pulping reactions were carried out in 50 mL and 100 mL or 1000 mL laboratory batch reactors. The simplest process technology was chosen for the laboratory experiments. The wood chips were generally cooked without any pre-wetting or pre-hydrolysis. The cooking liquor was not circulated. The concentration of the pulping medium was chosen according to the wood type. The closed reactors were heated in an oil bath to the desired temperature in 25 min and held at that temperature for 60–90 min.

Table 6. Parameters for the TCF Bleaching Sequence

Parameter	Unit	O	Q	EOP	Z_Q	P
Pulp	g atro	240	220	210	200	2×45
Consistency	% o.d.	10	5	10	10	10
Temperature	°C	90	80	90	50	90
Time	min	60	20	15 + 60	~/30	40 + 240
NaOH charge	% o.d.	1.47				1.25
pH		12.2	5	10.9	2.4/5	11.5
Oxygen pressure	bar	4.0		4.0		
EDTA	%		0.5		~/0.2	
DTPA	%					0.2
$MgSO_4$	%					0.2
H_2O_2 charge	%			1.0		2.0
Ozone charge	%				0.4/0.6	

Some larger scale experiments were carried out in an 18 L cooking plant at Impco-Voest-Alpine with pre-steaming the wood chips before cooking and the pulping liquor being circulated during cooking.

In the laboratory, separation of the black liquor and washing of the pulp were carried out by filtration. At Impco Voest-Alpine centrifugation was used. The pulps were air-dried.

The TCF bleaching sequence consisted of oxygen, peroxide, and ozone stages with interim washing in an O-Q-EOP-Z_Q-P sequence. The O, EOP and Z_Q steps were carried out in a Quantum-Mixer Mark V, the washing (Q) was done in a beaker in a water bath, and P was done in a Teflon reactor. The parameters are presented in Table 6.

Fiber Characterization

The kappa-numbers of the pulps were determined according to DIN 54 357. The viscosity of the pulp was determined in dilute cupriethylenediamine (CED) solution according to SCAN-CM 15 : 88. The ISO-brightness (ISO 3688/2470) was measured by Datacolor, Electropho 2000.

The mechanical properties of the fibers were measured at Holzforschung Austria. A standard laboratory Jokro refiner was used for beating (ÖN EN 25 264-3), Sheets were prepared according to Rapid-Kithen (DIN 54358 71). The grammage was measured in accordance with DIN ISO 536, tensile strength in accordance with DIN 53 112 Part 1, and tear strength in accordance with ÖN EN 25264-3.

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