PAPERMAKING FIBERS FROM GIANT REED (*ARUNDO DONAX* L.) BY ADVANCED ECOLOGICALLY FRIENDLY PULPING AND BLEACHING TECHNOLOGIES

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The anatomical structure and chemical composition of the stem-wall material of giant reed is considered from the viewpoint of raw material characterization for industrial fiber production. The effect of stem morphology (nodes and internodes) on pulping results and general pulp properties is discussed. The advantages of application of modern organic solvent based (organosolv) pulping technologies to giant reed are shown in comparison with the conventional (kraft) method. The conditions optimization for Ethanol-Alkali pulping (a selected organosolv pulping process) is given, and the chemical kinetics of the principal macromolecular components during ethanol-alkali pulping is described. The bleachability of organosolv pulps by short totally chlorine free (TCF) bleaching sequences using hydrogen peroxide and ozone as the active bleaching chemicals without pulp pre-delignification is examined and compared with kraft pulps. The enzymatic pre-treatment of reed organosolv pulps by commercial xylanase preparation is considered as a possibility toward the improvement of pulp bleachability.

Keywords: Arundo donax L.; Giant reed; Non-wood fibers; Organosolv pulping; Totally chlorine free (TCF) bleaching; Biobleaching; Bleach boosting

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INTRODUCTION

Non-woody plants are an important alternative source of fibers for the pulp and paper industry. The role of agro-fiber biomass is particularly prominent in countries with limited wood resources. In some regions of Asia, Africa and Latin America this is the only source of industrial papermaking fibers (Atchison 1993). The need to prevent the fast global deforestation (particularly in North America) and/or to meet the re-orientation of the West European agriculture towards non-food crops, due to general food overproduction, stimulated a recent renewed interest in agro-fiber plants (Van Dam et al. 1994; Moore 1996). A number of new fiber crops (such as elephant grass and reed canary grass) and traditional long-fiber species (such as flax and hemp) were recently (re)investigated for prospective industrial utilization (Leminen et al. 1996).

A widely distributed, naturally growing perennial rhizomatous grass, giant reed (*Arundo donax* L.), is a well-known fiber crop, the papermaking potential of which is being intensively reconsidered now. It has specific features, such as an annual harvesting period, high biomass productivity (up to 37 t $year^{-1}$ ha^{-1}, Vecchiet et al. 1996), ability to be intensively cultivated (Dalianis et al. 1994) and easy adaptability to different climatic

and soil conditions (Perdue 1958) which make *A. donax* one of the more promising industrial crops.

The history of *A. donax* application for papermaking started in 1830, when the first pulps were made by the boiling of stem material in calcium hydroxide (Perdue 1958). The comprehensive study of the pulping and bleaching ability of giant reed using traditional kraft and soda processes and chlorine-based bleaching was carried out between 1930-1950. The pulps were produced with rather low yield, but with satisfactory strength properties and bleachability (Jayme et al. 1948; Bhat and Virmani 1951; Di Felippo 1955).

Recently, the Nile Fiber Group Inc. (Washington, USA) together with Samoa Pacific Cellulose (California, USA) announced a successful commercial pulp run using exclusively *A. donax* reed (Nile Fiber Group 2002). The totally chlorine free (TCF) bleached kraft pulps were produced from reed growing wild in southern California using existing chemical wood pulping facilities of the Samoa Pacific mill. The new wood-free *A. donax* pulp is planned to be marketed under the name Samoa Cane.

The environmental and economical concern of pulp and paper manufacture, related to conventional pollutant sulfur- and chlorine-based industrial pulping and bleaching technologies, led to a generation of new approaches with reduced negative ecological impact. The pulping methods based on organic solvents in the reaction solution (organosolv pulping) and the bleaching methods based on non-chlorine oxidative chemicals (TCF bleaching) are the real commercially proved alternatives to traditional technologies (Stockburger 1993; Reeve 1996).

In the present article, the possibilities of papermaking fiber production from *A. donax* using organosolv pulping technologies in combination with TCF bleaching are reported based on our accumulated research experience in this field.

EXPERIMENTAL

Materials

The stems of giant reed (*A. donax*), free of leaves, with origin from Athens, Greece were used in this study. *A. donax* was cultivated in a university experimental plantation (Agricultural Engineering Department, Agricultural University of Athens), without irrigation, and was harvested with an average stem height of 4 m. For pulping, the stems were manually cut up to the approximate size of industrial chips (or match size - for kinetic and pulping optimization studies) and the moisture content was determined according to TAPPI standards. For chemical analysis a small portion of chips was additionally ground and screened to uniform particle size of 40-60 mesh.

Methods

Extractives were determined gravimetrically after extraction in a Soxhlet apparatus. Ash and silica (as SiO_2) were quantified according to TAPPI T15 os 58 and TAPPI T 245 om-94, respectively. Hemicelluloses were extracted from chlorite holocellulose by aqueous alkaline solutions and the insoluble residue was accepted as α-cellulose (Browning 1967). Carbohydrate composition was analyzed by GC as alditol-

acetate derivatives of monosaccharides after Saeman hydrolysis (Saeman et al. 1963). Lignin was determined as Klason and acid-soluble according to T 222 om-88 and UM 250 TAPPI, respectively.

The anatomical structure of the stem-wall material was examined by light microscopy of transverse sections (ca. 17 μm thickness, Reichert sliding microtome) and dissociated elements (macerated in acetic acid-hydrogen peroxide solution at 60ºC for 48 hours), as described elsewhere (Shatalov et al. 2001).

Pulping experiments were carried out in a 7-l laboratory-scale batch reactor with forced circulation of cooking liquor and automatic time-temperature and pressure control (Shatalov and Pereira 2001). Kinetic studies as well as cooking conditions optimization were performed in 100 ml stainless steel autoclaves rotated in an oil bath, using 10 g (on oven-dry base) material on each pulping (Shatalov and Pereira 2004a, 2004b). Kappa number of pulps was determined according to TAPPI T 236 cm-85. Pulp viscosity was measured in cupri-ethylenediamine (CED) solution according to SCAN-CM 15:88. Handsheet formation for physical and reflectance test of pulps was performed according to TAPPI T 205 om-88 and TAPPI T 272 om-92, respectively. Papermaking properties of pulp handsheets were examined according to TAPPI T 220 om-88. Pulp optical properties, i.e. ISO brightness and DIN 6167 C/2 yellowness index, were measured with a CM-3630 Spectrophotometer (Minolta).

Hydrogen peroxide bleaching (P-stage) as well as pulp chelating (Q-stage) and alkaline extraction (E-stage) were performed in sealed plastic bags plunged into an agitated water bath with temperature control. Low consistency ozone bleaching (Z-stage) was performed in a 2-l glass reactor (Fischer), equipped with a power stirrer and connected with a laboratory ozone generator (Fischer 502) (Shatalov and Pereira 2005, 2006a). Enzymatic pulp pre-treatment was carried out in the double-layer plastic bags incubated in a water bath under required temperature (Shatalov and Pereira 2006b).

RESULTS AND DISCUSSION

Giant Reed as a Raw Material for Fiber Production

Only the stems of *A. donax* are of interest for economically feasible fiber production on a commercial scale. The stem is morphologically heterogeneous and consists of hollow internodes and solid nodes, composed of nodal diaphragm (i.e., residual fragments of fundamental tissue – the pith) and adjacent transition regions (Fig.1).

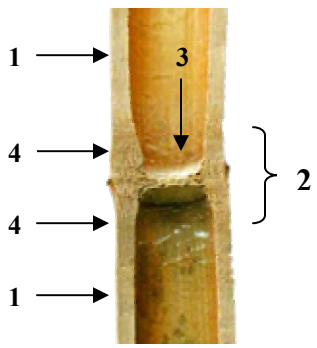
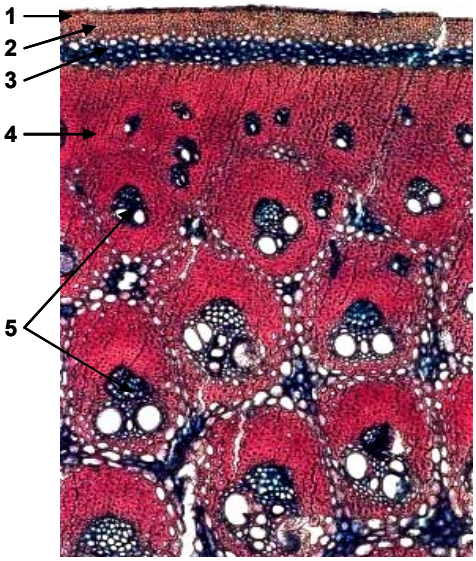


Fig. 1. Longitudinal cross-section of the *Arundo donax* L. culm: 1 - internode; 2 - node; 3 - nodal diaphragm; 4 - transition region (Shatalov and Pereira 2002a).

These botanically distinct parts can have different response on chemical processing. The anatomical and chemical analysis was therefore performed both with nodes and internodes, and the effect of stem morphology on general pulp properties has been examined using conventional kraft pulping, as a predominant process.

Anatomical structure and fiber morphology

An anatomical analysis showed similarity in the cellular structure of nodes and internodes (Shatalov and Pereira 2000a; Shatalov et al. 2001). The light microscopy of transverse sections revealed the prevalence of three tissue systems (Fig. 2): epidermal (or cortical parenchyma), fundamental (or ground parenchyma) and vascular (composed of fibro-vascular bundles).



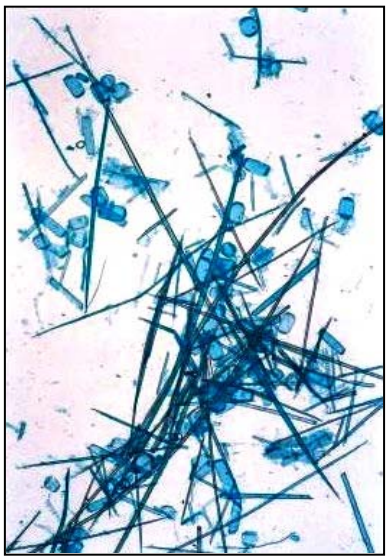


Fig. 2. (left) Transverse section of the internode of *A. donax* culm (100x): 1 - epidermis; 2 - strongly sclerified parenchyma cells; 3 - cortical parenchyma; 4 -fibers; 5 - fibro-vascular bundle.

Fig. 3. (right) Macerated sample of the internode of *A. donax* culm (100x) with fibers and parenchyma cells.

The average content of parenchyma in *A. donax* (57.8%) differs significantly from wood (7% and 20% for soft- and hardwood, respectively, Rydholm 1976) and resembles wheat straw and cornstalks (68% and 50%, respectively, Atchison 1993). The proportion of vascular tissue and fibers in *A. donax* (6.3% and 35.9%, respectively) is also different from woods (30% and 50% for hardwoods, Rydholm 1976), but close to other grasses, e.g., wheat straw (13.5% and 37.5%) and bamboo (11% and 38%). Thus, in comparison with woody raw materials, *A. donax* is poorer in fibers and richer in short parenchyma cells.

Biometric analysis of fibers (performed on macerated samples, Fig. 3) revealed some differences in fiber dimensions of nodes and internodes (Shatalov and Pereira 2000a; Shatalov et al. 2001). The fibers from internodes have equal length (1.2 mm) and smaller diameter (14.6 vs. 16.9 μm) and cell wall thickness (4.6 vs. 5.3μm), suggesting better papermaking properties, as compared to fibers from nodes. The average fiber

length of *A. donax* is fairly close to *Eucalyptus globulus* L. wood (0.7-1.3 mm) and resembles esparto (1.5 mm), wheat straw (1.0 mm) and bagasse (1-1.5 mm). The fiber width of *A. donax* is close to that reported for some eucalypts (13-19 μm) and resembles wheat straw (15 μm) and cornstalks (18 μm) (Atchison 1993). The fiber wall thickness of *A. donax* does not vary significantly from woods (2-8 μm) and is close to wheat straw (4 μm). Thus, the fiber biometry of *A. donax* (which directly correlates with strength properties of produced paper sheets) is very close to that of such world leaders of wood and non-wood pulp market as eucalypt wood and wheat straw, respectively.

Table 1. Results of Comparative Chemical and Anatomical Analysis of Nodes and Internodes of the *A. donax* Stem (Shatalov et al. 2001).

	Node	Internode
Ash (% o.d. reed)	4.77	6.14
- silicates	1.31	1.16
Extractives (% o.d. reed)	13.04	11.16
- dichloromethane	0.46	0.37
- ethanol	5.88	4.18
- hot water	6.70	6.61
Lignin (% o.d. reed)	20.92	21.31
- Klason	19.03	19.60
- acid-soluble	1.89	1.71
Holocellulose (% o.d. reed)	61.21	61.41
- α-cellulose	29.18	32.93
- hemicelluloses	32.03	28.48
Parenchyma (%)	55.8	59.8
Fibre (%)	37.9	33.9
Vascular tissue (%)	6.4	6.2
Fibre length (mm)	1.2	1.2
Fibre width (μm)	16.9	14.6
Fibre wall thickness (μm)	5.3	4.6

Chemical composition

The comparative analysis of chemical composition revealed some differences between nodes and internodes (Shatalov and Pereira 2000a; Shatalov et al. 2001). With close lignin content (ca. 21%), the nodes are richer in extractives (13.04 vs. 11.16%) and hemicelluloses (32.0 vs. 28.5%) and poorer in cellulose (29.2 vs. 32.9%), as compared with internodes. Generally, the chemical analysis resembled the typical characteristics for other grasses and deviations from wood. Obviously, *A. donax* contains considerably less lignin and cellulose than woods (24-34% and 38-50%, respectively, Rydholm 1976), but is comparable in hemicelluloses. Similar to other grasses, *A. donax* showed remarkable predominance of pentosans over hexosans (96% vs. 4% of hemicelluloses) and the prevalence of xylan over other non-cellulosic polysaccharide (ca 90% of total). One other difference from wood was found in the relatively high content of ash and extractives, which is also common for grasses.

Effect of stem morphology on pulp and paper properties

Different kraft pulping properties of nodes and internodes were established in accordance to the difference in chemical composition and anatomical structure (Shatalov and Pereira 2002a). The pulps with higher screened yield (44.5 vs. 38.6%) and lower content of residual lignin (Kappa number 25 vs. 33) were produced from internodes, as compared with nodes. The papermaking properties as well as brightness of unbeaten kraft pulps from internodes were also higher (Table 2). Thus, the internodes are more suitable for pulping and the presence of nodes has an adverse affect on pulp yield and properties.

Table 2. Results of Kraft Pulping and Papermaking Properties of Unbeaten Pulps from Nodes, Internodes and the Whole Stems of *A. donax* L. (Shatalov and Pereira 2002a).

	Node	Internode	Whole stem
Yield (% o.d. reed) - Screened yield - Rejects	43.0 38.6 4.4	44.7 44.5 0.2	43.8 42.1 1.7
Klason lignin (% o.d. reed)	4.2	3.2	3.3
Kappa number	33	25	26
Viscosity number (ml g^{-1})	1054	1156	1135
Burst index (kPa·m^2 g^{-1})	0.2	0.7	0.5
Tensile index (N·m g^{-1})	5.2	25.2	17.4
Tear index (mN·m^2 g^{-1})	4.4	13.3	10.5
Brightness (% ISO)	21.2	23.9	22.8

The results for the whole stem pulping (as the more useful option for practical reasons) are similar or somewhat lower than those for internodes, reflecting the mass proportion of nodes and internodes in the stem.

Organosolv Pulping

Comparison of different organosolv technologies

Four different acid- and alkali-based organosolv pulping technologies, which are now under different stages of commercial development, were used to examine the pulping ability of *A. donax*: Alkali-Sulfite-Anthraquinone-Methanol (ASAM), Alkali-Anthraquinone-Methanol (Organocell), Ethanol-Alkali and Peroxyacids (Milox) (Shatalov and Pereira 2000a, 2000b, 2001). The autocatalyzed ethanol pulping of *A. donax* (Repap process) is under investigation now, and the results are not presented here. All methods were applied using standard conditions reported for pulping of similar crops or hardwood (Table 3). Conventional kraft pulp was used as a reference.

The comparative study showed a high accessibility of *A. donax* to organosolv delignification. Bleachable grade pulps with high yield (47-52% for organosolv vs. 44% for kraft), ISO brightness (25-37% ISO for organosolv vs. 23% ISO for kraft) and intrinsic viscosity (885-1192 ml g^{-1} for organosolv vs. 1135 ml g^{-1} for kraft), good mechanical properties and low content of residual lignin were produced (Table 4). The results of Ethanol-Alkali and ASAM pulping were particularly promising. The properties

of these organosolv pulps were superior to kraft pulps and comparable with those of industrial hardwood kraft pulp (e.g. *E. globulus*). The remarkably high brightness of Ethanol-Alkali and ASAM pulps (36.5% ISO and 37.1% ISO, respectively) suggested easy pulp bleachability using short bleaching sequences with reduced chemical charge.

Table 3. Pulping Conditions.

	ASAM	Organocell	Ethanol-Alkali	Milox	
				Stage 1	Stage 2
Alkali charge (% o.d.m.)	-	20	25	-	-
Chemical charge (% o.d.m.)	20	-	-	-	-
Active alkali (%, as Na_2O)	-	-	-	-	-
Sulfidity (%, as Na_2O)	-	-	-	-	-
Solvent content (% by vol.)	30	30	40	-	-
AQ (% o.d.m.)	0.1	0.1	-	-	-
Formic acid/acetic acid/water (% by vol.)	-	-	-	60/20/20	60/20/20
H_2O_2 charge (% o.d.m.)	-	-	-	3	-
Liquor-to-material ratio (ml g^{-1})	5/1	5/1	5/1	4/1	8/1
Pulping temperature (ºC)	175	170	140	90	100
Pulping time (min)	100	90	180	180	120

Table 4. Results of Organosolv Pulping of *A. donax* as Compared with Kraft.

	ASAM	Organocell	Ethanol-Alkali	Milox	Kraft (ref.)
Yield (% o.d.m.)	47.7	50.2	47.4	52.4	43.8
- Screened	46.8	46.6	47.0	51.9	42.1
Brightness (% ISO)	37.1	26.5	36.5	24.9	22.8
Viscosity (ml g^{-1})	1192	885	1140	1042	1135
Kappa number	22	26	21	30	26
Klason lignin (% o.d.m.)	2.6	2.7	2.5	3.6	3.3
Burst index (kPa m^2 g^{-1})	0.9	1.0	1.7	0.6	0.5
Tensile index (N m g^{-1})	14.1	16.9	27.9	14.2	17.4
Tear index (mN m^2 g^{-1})	10.5	9.2	11.4	7.1	10.5

Pulp beating using a laboratory PFI mill showed that the strength properties of reed organosolv pulps (particularly of Ethanol-Alkali pulp) can be substantially improved with minimal energy requirements on beating (Shatalov and Pereira 2000b, 2001). The maximal bursting and tensile strength can be easily reached at 1000 PFI rev. (2000 PFI rev. is required for kraft eucalypt pulp to reach the same values, Valente et al. 1991). At the same time, even moderate beating of organosolv reed pulps (up to 2000 PFI rev.) leads to a dramatic increase in drainage resistance to 60-70º SR, thereby causing serious dewatering problems (Shatalov and Pereira 2001).

Ethanol-enhanced alkaline pulping

Based on the results of comparative studies on pulping efficiency, the Ethanol-Alkali pulping (Ethanol-enhanced or Ethanol-reinforced alkaline pulping) was selected as a sulfur-free organosolv process having more potential for *A. donax*. The influence of process variables on yield and properties of Ethanol-Alkali pulps has been examined to

identify the optimal pulping conditions and the kinetics of lignin and carbohydrate degradation during Ethanol-Alkali delignification.

Pulping conditions optimization. The effect of such cooking variables as alkali charge (5-35% on o.d. reed), ethanol content (20-60% by vol.), liquor-to-reed ratio (5-8 ml/g), cooking time (5-240 min) and cooking temperature (130-150ºC) was examined (Shatalov and Pereira 2002b,c; 2004a,b). The alkalinity of the aqueous phase was found to be a controlling factor of Ethanol-Alkali delignification, strongly affecting pulping results. About 82% of lignin was removed and pulp yield fell to 49% with a rise in alkali concentration up to 25%. Ethanol addition to alkaline pulping solution improved substantially the selectivity of delignification (through suppression of degradation reactions of carbohydrates and prevention of lignin condensation reactions, Shatalov and Pereira 2002b). With a rise in ethanol content in the reaction mixture from 20 to 60% (by vol.), the yield of ethanol-alkali pulps increased by about 5%, while the content of residual lignin decreased by 10%. The intensity of these processes was more notable with ethanol content up to 40%. The change of the liquor-to-reed ratio (L/S) within an economically reasonable range of 5-8 ml g^{-1} did not reveal any noticeable effect on pulping results, while the subsequent reduction of L/S ratio on pulping is undesirable because of an impaired diffusion of chemicals. The presence of ethanol in the alkaline pulping solution allowed using rather low temperatures for delignification. About 90% of lignin can be removed with 180 min pulping at 140ºC. Under these gentle conditions, the degradation of polysaccharides was reduced to a minimum, providing fairly high values of screened pulp yield of 45-48%.

Kinetics of lignin and polysaccharide degradation. A novel original approach for kinetic description of lignin and polysaccharide degradation during chemical pulping has been developed and applied (Shatalov and Pereira 2004c; 2005a,b,c).

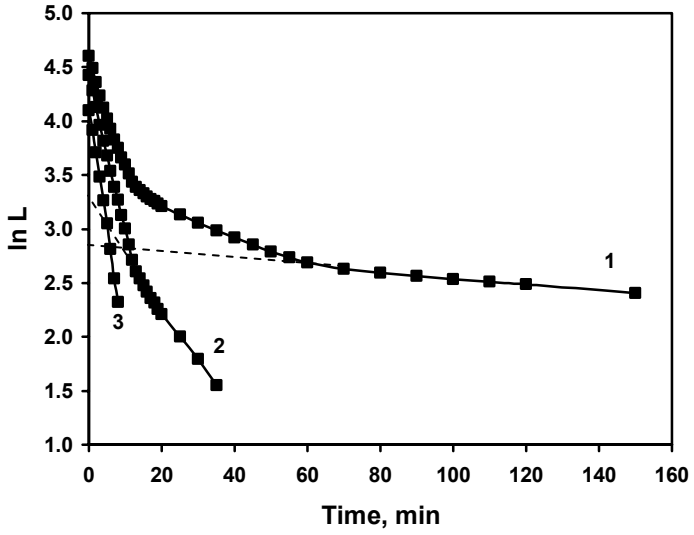


Fig. 4. Kinetic curves of ethanol-alkali delignification of *A. donax* (140ºC):1-experimental LnL=Ln(L_1+L_2+L_3)=f(t); 2-calculated Ln(L-L_3)=Ln(L_1+L_2)=f(t); 3-calculated Ln(L-L_3-L_2)=LnL_1=f(t); L_1,L_2,L_3 - lignin fractions.

Based on properties of a multi-component reaction system, the degradation of lignin as well as carbohydrates was considered as a complex of *n*-parallel irreversible first-order reactions with similar final product. The successive elimination from the semi-logarithmic anamorphous of kinetic curve of the contributions from the individual polymer structures, or groups of polymer structures with close reactivity (as a kinetically homogeneous system) allowed estimating accurately the kinetic heterogeneity of delignification and quantifying the lignin or carbohydrate fractions with distinguishable reactivity.

Three lignin fractions of *A. donax* were revealed and quantified in proportions of approximately 61, 23 and 16% (Fig. 4). The proportion of lignin fractions was different from that reported for wood, but close to another crop – wheat straw, where the first more reactive lignin fraction was also found as a major fraction (about 90%). The values of apparent activation energy were estimated respectively as 64, 89 and 96 kJ mol^{-1}, and were generally within the range of those reported for wood kraft and organosolv pulping. The simulation of Ethanol-Alkali delignification using the calculated kinetic parameters showed the high reproducibility of experimental data on lignin removal. The data reproducibility was substantially higher in comparison with that obtained by conventional consecutive kinetic model (sum of square residuals (SQR) 0.0036 vs. 0.0856, Shatalov and Pereira 2005a) (Fig.5).

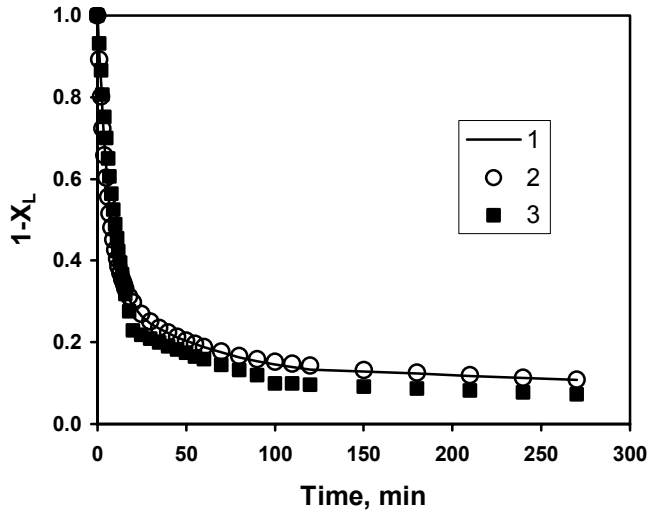


Fig. 5. Data fitting on lignin conversion: 1-experimental kinetic curve; 2-kinetic curve simulated by new model; 3-kinetic curve simulated by traditional model.

The degradation of polysaccharides was accurately described in terms of two kinetically homogeneous fractions. Total polysaccharide losses during Ethanol-Alkali pulping of *A. donax* result mainly from the fast removal of the first more reactive xylan and cellulose fractions (48 and 4%, respectively, Shatalov and Pereira 2005b). The degradation of the second fractions slowly proceeded through pulping with two to three orders lower rate. The apparent activation energies were estimated as 74.4 and 140.9 kJ mol^{-1} - for xylan fractions and 105.2 and 106.5 kJ mol^{-1} - for cellulose fractions. The degradation kinetics of minor *A. donax* carbohydrates (composed of arabinosyl,

galactosyl and mannosyl residuals) and uronic acid moieties during ethanol-alkali pulping was also studied (Shatalov and Pereira 2005c).

Hexenuronic acids. The unsaturated 4-deoxy-β-L-*threo*-hex-4-enopyranosyl-uronic acid (hexenuronic acid or HexA) formed from 4-*O*-methylglucuronic acid (MeGlcA) side groups of heteroxylan by β-elimination of methanol during alkaline pulping was shown to have harmful effect on subsequent pulp bleaching through the increased consumption of bleaching chemicals, decreased brightness and increased brightness reversion, poor metal removal, and formation of calcium oxalate deposits in the bleaching equipment. It was of special interest to examine the effect of organic solvent (ethanol) addition on the chemical behavior of HexA during alkaline pulping of *A. donax*. It was shown (Shatalov and Pereira 2003a, 2004d) that in ethanol-alkali reaction medium under pulping conditions about 90% of the initial uronic acid (UA) moieties of *A. donax* (composed mainly of MeGlcA side groups attached to heteroxylan) are degraded. At the end of the process, the residual MeGlcA in pulp are 84% converted to HexA. The maximal detected content of HexA in pulp was 30 μmol g^{-1}. No appreciable degradation of HexA during the course of pulping (under the temperature range of 130-150ºC) was observed. The overall rate of UA degradation was one order higher than the rate of UA conversion to HexA. The reaction medium alkalinity was found as a controlling factor for UA and HexA stability during pulping. The addition of organic solvent had a similar, but less notable, effect on UA and HexA stability. The kinetics of UA degradation as well as of HexA formation were accurately described in terms of three simultaneous first-order reactions, corresponding to three kinetically homogeneous fractions (Shatalov and Pereira 2003a, 2005c). The degradation of the first two uronic acid fractions (about 50% of total UA) as well as the formation of the first two hexenuronic acid fractions (about 63% of total formed HexA) proceeds with similar rates and is completed within the first-third of pulping time. The last (less reactive) HexA fraction is formed with one-order lower rate than the degradation rate of the last UA fraction.

TCF Bleaching of Organosolv Pulps

Based on the results of the comparative study on organosolv delignification of *A. donax* (Shatalov and Pereira 2001), three alkali-based organosolv pulps, i.e., ASAM, Organocell and Ethanol-Alkali, were chosen for subsequent bleaching experiments. Kraft pulp from *A. donax* was used as a reference.

Peroxide bleaching

All of the tested pulps were bleached with a simple three-stage peroxide sequence QPPP (where Q - chelating treatment and P - hydrogen peroxide bleaching stage), without oxygen pre-delignification (Shatalov and Pereira 2003b, 2005d). The conditions applied were identical for each P-stage and are summarized in Table 5. The pulp chelating with EDTA was done before bleaching to remove transition metals. There were some additional chemicals used (Epsom salt and DTPA) to prevent radical-induced degradation of carbohydrates.

The brightness level of ca. 76-78% ISO was reached for all organosolv pulps (Table 6), irrespective of the starting brightness. It was somewhat higher than that

reported for oxygen-delignified peroxide bleached soda-AQ reed pulp (75% ISO brightness, Basta et al. 2002) and oxygen-delignified QPPP-bleached acetosov pine and eucalypt pulps (67-70% ISO brightness, Vázquez et al. 2002). The peroxide consumption varied for different pulps and was directly related to starting pulp brightness.

Table 5. Conditions of hydrogen peroxide bleaching.

	Q-stage	P-stage
Pulp consistency (%)	3	10
Temperature (°C)	70	90
Time (min)	60	180
H_2O_2 charge (% o.d. pulp)	-	3.0
NaOH charge (% o.d. pulp)	-	1.5
EDTA charge (% o.d. pulp)	0.3	-
DTPA charge (% o.d. pulp)	-	0.2
$MgSO_4$ charge (% o.d. pulp)*	-	0.3
pH initial**	4.5	-
pH final***	-	10.0-10.40
* Magnesium sulfate was applied as $MgSO_4 \cdot 7H_2O$; ** pH was adjusted by diluted sulfuric acid		
*** pH value varies with stage and pulp sample		

Table 6. Properties of peroxide bleached reed organosolv and kraft (ref.) pulps.

	Ethanol-Alkali	ASAM	Organocell	Kraft (ref.)
Yield (%)	93.2	90.2	90.6	91.9
H_2O_2 consumption (%)	60.0	68.9	82.2	74.4
Lignin (% o.d. pulp)	2.15	1.68	1.48	1.99
- Klason	0.78	0.72	0.50	0.89
- Acid-soluble	1.37	0.96	0.98	1.10
Intrinsic viscosity (ml g^{-1})	1111	973	788	842
Brightness (% ISO)	76.4	77.0	77.6	75.4

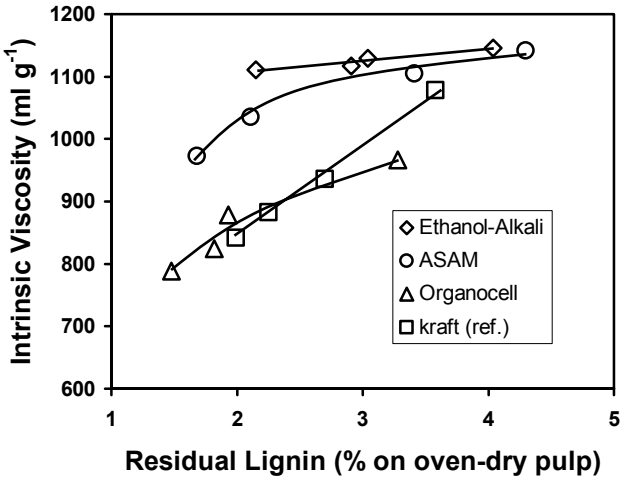


Fig. 6. Selectivity of peroxide bleaching of *A. donax* organosolv pulps (Shatalov and Pereira 2005d).

All organosolv pulps (particularly Ethanol-Alkali) showed substantially higher bleaching selectivity in comparison with kraft (Fig. 6). The viscosity loss of only 3% after complete bleaching was noted for Ethanol-Alkali pulp vs. 22% for kraft. The bleaching efficiency with respect to lignin removal, assumed as a measure of pulp bleachability, was also higher for reed organosolv pulps (Fig. 7). The delignification of ASAM pulp was more intensive (ca. 60% lignin removal), followed by Ethanol-Alkali and Organocell. The lignin removal from kraft pulp was poorer (ca. 40%), despite the highest brightness improvement per unit of bleaching chemical consumed (Shatalov and Pereira 2005d). Thus, no correlation between brightening and delignifying effect was observed during peroxide bleaching of *A. donax* pulps.

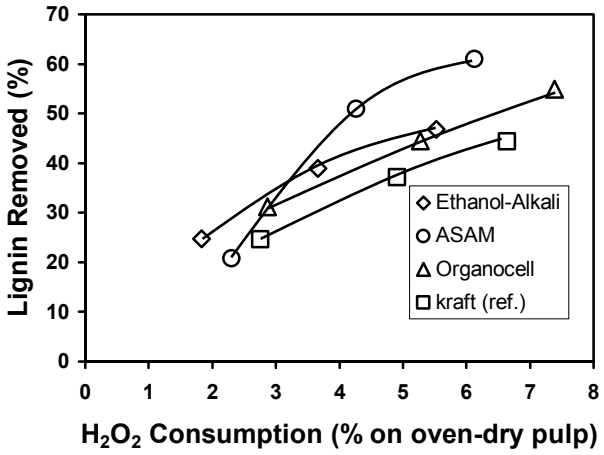


Fig. 7. Delignification efficiency of peroxide bleaching of *A. donax* organosolv pulps (Shatalov and Pereira 2005d).

The papermaking properties of bleached organosolv pulps after PFI beating were found superior (or close) to those of kraft pulp, in contrast to unbleached pulps where the improvement of kraft pulp properties with beating was definitely higher (Shatalov and Pereira 2001).

Ozone-based bleaching

To consider the possibility of brightness improvement, the introduction of an ozone-stage within a short TCF sequence was studied (Shatalov and Pereira 2005e, 2006a). The ASAM, Organocell and Ethanol-soda pulps were bleached by AZE_RQP (actually ZEP) bleaching sequence without oxygen pre-bleaching, and compared with conventional kraft pulp (where A - acidic pulp pre-treatment, Z - ozone stage, E_R - alkaline extraction in the presence of reducing agent, Q - pulp chelating, P - hydrogen peroxide stage). The specific bleaching conditions are listed in Table 7.

The introduction of an ozone-stage into the bleaching sequence resulted in an appreciable gain in brightness and degree of delignification in comparison with the three-stage peroxide bleaching (Table 8). The brightness was improved by 7.3; 5.8 and 2.0 points, respectively for Ethanol-Alkali, Organocell and ASAM pulps and showed the maximal values of 83.7% ISO; 83.4% ISO and 79.4% ISO, respectively, vs. 79.6% ISO

for kraft pulp. The removal of Klason lignin (which directly correlates with kappa number) by 83%, 77% and 69% was noted respectively for Organocell, Ethanol-Alkali and ASAM pulps, vs. 69% for kraft pulp. The reduction of ozonated pulps before alkaline extraction allowed limiting carbohydrate degradation with loss in intrinsic viscosity by only 11-18% for organosolv pulps, vs. 21% for kraft pulp (Shatalov and Pereira 2006b).

Table 7. Conditions of AZE_RQP bleaching.

	A	Z	E_R	Q	P
Pulp consistency (%)	3	3	10	3	10
Temperature (^oC)	20	20	60	50	90
Time (min)	30	20	60	50	90
O_3 (% on oven-dry pulp)	-	0.8	-	-	-
H_2O_2 (% on oven-dry pulp)	-	-	-	-	2.5
NaOH (% on oven-dry pulp)	-	-	1.0	-	1.5
EDTA (% on oven-dry pulp)	-	-	-	0.3	-
DTPA (% on oven-dry pulp)	-	-	-	-	0.2
$MgSO_4$ (% on oven-dry pulp)*	-	-	-	-	0.3
$NaBH_4$ (% on oven-dry pulp)	-	-	0.1	-	-
pH **	2.0	2.0	-	4.5	-
* Magnesium sulfate was applied as $MgSO_4 \cdot 7H_2O$; ** pH was adjusted by diluted sulfuric acid					

Table 8. Properties of AZE_RQP-bleached organosolv and kraft (ref.) pulps from *A. donax.*

	Ethanol-Alkali	ASAM	Organocell	Kraft (ref.)
Yield (%)	93.4	91.0	90.9	92.1
Lignin (% o.d. pulp)	1.65	1.89	1.26	1.66
- Klason	0.57	0.96	0.36	0.79
- Acid-soluble	1.08	0.93	0.90	0.87
Intrinsic viscosity (ml g^{-1})	988	1009	789	852
Brightness (% ISO)	83.7	79.4	83.4	79.6
Burst index (kPa m^2 g^{-1})	1.32	1.30	1.27	1.11
Tensile index (N m g^{-1})	15.85	15.28	14.26	12.38
Tear index (mN m^2 g^{-1})	9.16	9.02	8.54	8.84

The pulp bleachability, in terms of improvement in brightness or lignin removal per unit of applied chemicals, was found to be higher for Organocell pulp. The ASAM and Ethanol-Alkali pulps showed the highest bleaching selectivity, expressed by viscosity loss per unit of lignin removed or brightness improved. The development of strength properties of PFI beaten kraft pulp was poorer in comparison with ASAM, but close or somewhat better (as in the case of tearing strength) to Ethanol-Alkali and Organocell pulps. The overall bleaching results of organosolv pulps from *A. donax* were superior to those of kraft (Shatalov and Pereira 2006a).

Enzyme-aided bleaching

The effect of enzymatic pre-treatment on the bleachability of *A. donax* organosolv pulps has been examined. The ASAM, Organocell and Ethanol-Alkali pulps were treated

with the commercial xylanase preparation Ecopulp TX-200A (AB Enzymes) and bleached by simple one-stage hydrogen peroxide bleaching. The enzymatic bleach boosting effect was examined and compared with conventional kraft reed pulp (Shatalov and Pereira 2006c, d).

The bleaching effect (i.e., direct brightening and delignification) was already observed during the enzymatic stage and led to a brightness increase by 0.6-1.0% ISO (more for Ethanol-Akali and Organocell) and lignin removal by 11% for organosolv pulps vs. 0.7% ISO and 14%, respectively, for kraft pulp. The xylanase pre-treatment substantially improved the subsequent chemical bleaching of reed organosolv pulps with hydrogen peroxide (Table 9).

Table 9. Properties of enzyme-treated organosolv pulps from *A. donax* after one-stage hydrogen peroxide bleaching.

	ASAM	Ethanol-Alkali	Organocell	Kraft (ref.)
Brightness (% ISO)	63.4(1.5)*	70.2(2.1)	64.4(2.9)	61.4(2.7)
Lignin (% o.d. pulp)	2.65(0.22)	2.55(0.29)	1.75(0.30)	1.59(0.33)
Intrinsic viscosity (ml g^{-1})	1144(29)	1140(41)	918(19)	907(21)
Peroxide consumption (%)	75.4(3.4)	39.7(2.2)	74.3(11.2)	92.7(5.1)
* The property improvement in comparison with control sample (without xylanase treatment) is shown in brackets				

The gain in brightness by 1.5-2.9% ISO under reduced consumption of active bleaching chemical by 2.2-11.2% (as a maximum for Organocell and a minimum for ASAM pulp) was observed. The degree of delignification and intrinsic viscosity of enzyme-treated organosolv pulps increased after peroxide bleaching by 7.7-14.9% and by 2.1-3.7%, respectively (Shatalov and Pereira 2006c). Thus, commercial xylanase preparation specifically designed to improve bleachability of industrial wood kraft pulps can be successfully applied to untraditional reed organosolv pulps. This gives the possibility to incorporate enzymatic stage into the TCF bleaching sequences and to increase thereby the final brightness ceiling of bleached pulps. The brightness level of 85-90% ISO (the fully bleached reed organosolv pulps) can also be achieved by reinforcement of the enzyme-aided TCF bleaching by highly effective catalytic systems of oxidative delignification.

CONCLUSIONS

A. donax (giant reed) possesses many of the qualities required for an ideal candidate to occupy leading positions on the world non-wood pulp market, and it provides an excellent alternative to wood fibers in meeting the rapidly growing demand for pulp and paper products. The high accessibility of *A. donax* to advanced ecologically friendly pulping and bleaching technologies makes it a particularly attractive and promising fiber source; especially in light of pressure against traditional industrial technologies toward more environmentally sound techniques.

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