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Final report

Bleaching of Sisal Pulp at Laboratory Scale

referring to

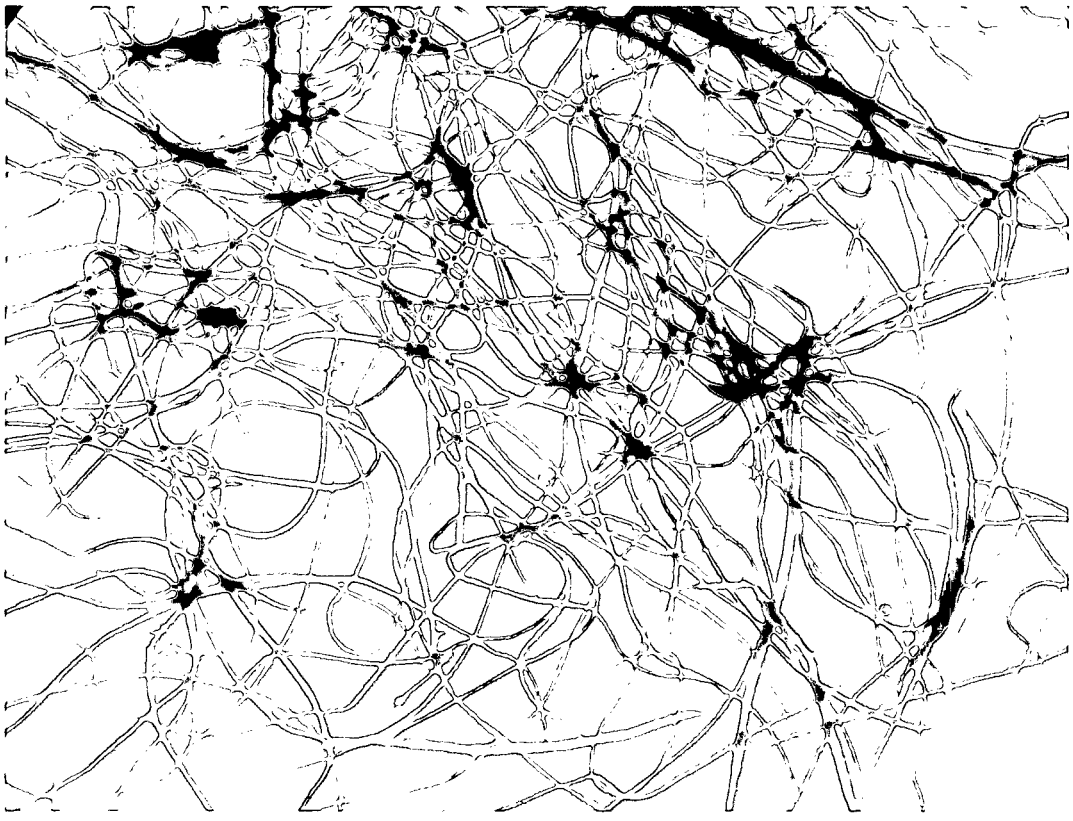
UNIDO Project FC/RAF/04/001
Product and Market Development of Sisal and Henequen

UNIDO Contract No. 2004/092

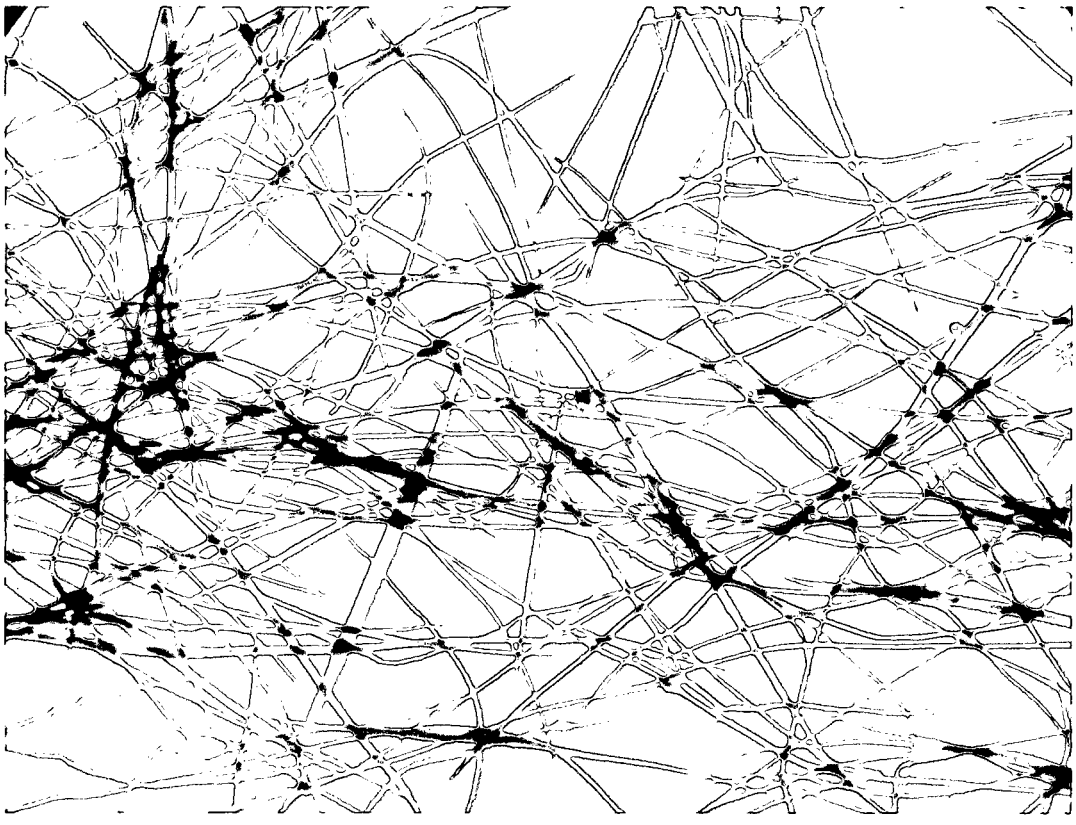
Project leader: **Tjasa Drnovsek, Ph.D.**

Period covered in report: **September 6 – November 9, 2004**
Date of report: **9. Januar 2005**

Ill. 1



Ill. 2



1. Content list

Page

2. Framework programe for the final report

Referring to the demands expressed in the Terms of Reference the following aims should be achieved:

A) evaluation of the pulping conditions for sisal fibres using the proposed cooking diagram with the results

B) performance of small scale bleaching trials of sisal pulp delivered by Unido according to ECF and TCF sequences and selection of the optimal conditions for both processes with respect to basic properties of bleached fibres

C) performance of the selected ECF and TCF bleaching trials of sisal pulp delivered by Unido to obtain enough bleached pulp for testing and preparing the sample sheets for presentation

D) performance of the selected ECF and TCF bleaching trials of sisal fibres (delignified at the Institute) with testing results

3. Methods and Analyses

Dry matter content	ISO 638 - 1978
Kappa number	ISO 302 - 1981
Brightness	ISO 3688 - 1977
Brightness stability	ISO 5630/1 - 1982
Limiting viscosity number	SCAN-CM 15:88
Residual alkali	SCAN-N 33:94
Ozone consumption	DIN 19627 - 1993
Preparation of laboratory sheets for physical testing-	
Conventional sheet-former method	ISO 5269-1 - 1998
Determination of physical properties	ISO 5270 - 1998
Average fibre length and coarsness (Kajaani FS)	Tappi 271 pm-91
Average fibre width	Handbuck Der Mikroskopie in der Technik, Band V, Teil 2, 1951
Dirt in pulp	T 213 om-89
Determination of pH of aqueous extract	ISO 6588 - 1995

4. Symbols used to characterize the bleaching stages:

O	oxygen
D	chlorine dioxide
E, Ep	extraction stage, e.s.reinforced by peroxide
P	peroxide stage
Q	chelation stage
A	acidification stage
Z	ozone stage: Z_h – high consistency, Z_l – low consistency
SO_2	washing with SO_2-water

5. Sisal fibres Pulping tests

Material:

Sisal fibres were prepared in a hammer mill and supplied by Unido.
Appearance of the material: The fibres were dry, short and bright, in a good conditions.
Dry matter content: 89.00 %

Pulping equipment:

A 10-l rotating digester with electric heating was used for delignification process.
700 g of o.d. sisal material was fed into the digester for one trial.

Chemicals:

The concentration of NaOH solution was 200 g/L
Antraquinone (Aq) was dry and of Bayer origin.

Cooking trials:

The digester and the sisal material were preheated before each trial to approx. 80 - 90°C.
Two cooking trials were conducted with different amounts of added Aq.
Cooking diagrams for both trials are listed in Table I. Results are included.

Sampling of cooking liquors:

A sample of cooking liquor was analysed for the rest of alkali after each trial.

Cleaning and Screening

The Wennberg laboratory strainer was used for pulp screening and cleaning after cooking. The yield was measured and sample sheets were prepared for analyses of kappa No, limiting viscosity No and ISO brightness.

Table I. Cooking conditions with basic results

Trial	PK1	PK2
Cooking chemicals:		
NaOH, %	13.5	13.5
Antroquinone, %	**0.1**	**0.01**
Material/liquor ratio	1:4	1:4
Diagram:		
Heating up time, min	90	90
$Temperature_{max}$,C	165	165
Time on $temperature_{max}$, min	75	75
Results:		
Kappa number	12.0	15.7
Total yield, %	72.7	72.9
Shives, %	0.12	1.66
Pulp yield, %	72.6	71.3
Active alkali in black liquor,	1.04	2.24
g/L	1.04	2.24
Alkali consumed, %	97.0	94.4
Brightness, %	32.8	32.2
Limiting viscosity No, mL/g	970	1015

6. Sisal pulp

The bleaching experiments were conducted with unbleached pulp delivered by UNIDO. The basic characteristics of pulp were:

Dry matter content, %	89.81
Kappa number	9.22
ISO Brightness, %	38.69
Limiting viscosity No, mL/g	572

6.2 Extended oxygen delignification stage

A 10l rotating digester with electric heating was used, the same as for delignification process. 500 g of o.d. sisal pulp were fed into the digester for one trial. before the process, the digester and the pulp were preheated to ca. 80 - 90°C. The procedure is presented in Table II. Results are included.

Table II. Oxygen stage procedure and results

Conditions:	
NaOH, %	1.5
$MgSO_4$, %	0.5
Oxygen pressure, bar	6
pH begin/end	12.3/10.9
Consistency, %	10
Reaction time, min	60
Temperature, ^0C	95
Results:	
Active alkali in spent liquor, g/L	15.2
Yield, %	94.9
Brightness, %	55.2
Micro kappa No	5.3

6.2 Small scale bleaching experiments

Small scale bleaching experiments for all stages were conducted in plastic bags (30 g o.d. pulp, each), immersed in water bath of certain temperature. Plastic bags with pulp suspensions were taken out of the water bath and periodically hand-mixed. At the end of the stage, pulp suspension was dewaterized; the rest of the chemicals were analysed in spent liquors. Fibres were washed and sample sheets were made for measuring the brightness level achieved after each stage; brightness stability and limiting viscosity number were measured only of final bleached fibres.

6.2.1 ECF bleaching trials

First, a DED sequence of unbleached pulp was tested with and without oxygen stage at the beginning of the sequence.
A DEpD sequence was tested only with unbleached pulp (without oxygen).
The bleaching conditions of all these trials are presented in Table III. Results are included.

Table III. Small scale ECF bleaching trials and some basic results

Trials	DED	ODED	DEpD
D_1-stage:			
ClO_2, as act.Cl added, %	2.0	1.5	2.0
pH, begin/end	6.0/6.4	6.3/6.7	2.2/3.3
Consistency, %	10	10	10
Temperature, C	50	50	50
Reaction time, min	60	60	60
Rest of Cl, %	0.008	0.19	0.02
Brightness, % ISO	74.2	82.2	
E, Ep*-stage:			
NaOH, %	1.0	1.0	1.0
H_2O_2, %			0.5
Rest of H_2O_2, %			0.1
pH, begin/end	11.9/11.1	11.9/10.9	11.3/11.1
Consistency, %	10	10	10
Temperature, C	50	50	50
Reaction time, min	90	90	90
Brightness, % ISO			82.5
D_2-stage:			
ClO_2, as act.Cl added, %	1.5	1.5	1.5
pH, begin/end	4.6/4.9	4.6/4.9	4.6/4.9
Consistency, %	10	10	10
Temperature, C	60	60	60
Time, min	180	180	180
Rest of Cl, %	0.05	0.05	0.05
End characteristics:			
Brightness, %	87.6	88.9	88.5
Brightness loss, %		2.0	
Lim. viscosity number, mL/g	507	479	522

* to the extraction stage, reinforced with peroxide, $MgSO_4$ (0.2 %) and DTPA (0.2 %) were added.

6.2.2 TCF bleaching trials

Selected TCF sequences were devided into three groups: with ozone stage (with (1.) and without (2.) oxygen at the beginning); without ozone stage and with oxygen at the beginning (3.).

Three bleaching agents were proposed: oxygen, ozone and peroxide. The oxygen stage is already described in Table II of this report; the small scale peroxide stage was conducted in plastic bags in water bath, the same as with ECF sequences. The ozone stage was carried out in a laboratory digester in a stainless steel-covered vessel with a gas input and output installed on the roof of the vessel. For the production of ozone gas a laboratory Ozone generator, produced by Erwin Sander Company, Germany, was available. The procedure was carried out according to the 19627 DIN standard.

6.2.2.1 TCF sequence without ozone

By means of the sequence **O(Q)P(Q)P** (without the ozone stage) only the oxygen pretreated pulp was selected for testing. The procedure of the sequence is given in Table IV. The characteristics of the end-bleached fibres are included.

6.2.2.2 TCF sequences with ozone

The second group of TCF sequences were made by combining all chlorine free bleaching chemicals: oxygen, ozone and peroxide. The oxygen treatement of pulp was the same as with previous trials. At acidification stage, the pulp has to be treated with hot diluted sulphur acid and without the in-between washing before the ozone stage. If further high consistency ozone is proposed, the pulp is dewaterized after the acidification stage until the target consistency is reached. A high consistency ozone stage was selected for the first series of trials. Only time varied. At the end of the ozone stage, the pulp was washed and the final peroxide stage was carried out – equal for all ozone "time-variant" samples. The conditions and results for the OAZ_hP sequences are shown in Table V; for the AZ_hP series in Table VI; and for the OAZ_lP series in Table VII.

Table IV. TCF sequence O(Q)P(Q)P – the procedure and the basic results

Oxygen stage:	
Already described in Table II.	
Q-chelation stages:	
Consistency, %	10
Temperature, ^{0}C	60
Time, min	60
Acidification with H_2SO_4 to pH	5-5.5
DTPA, %	0.2
Actual pH, begin/end	5.1/6.7
P_1-stage:	
H_2O_2, %	2.0
NaOH, %	1.5
$MgSO_4$, %	0.2
DTPA, %	0.2
Consistency, %	10
Temperature, ^{0}C	70
Time, min	180
pH, begin/end	10.9/10.9
Rest of peroxide, %	0.65
Brightness, %	79.1
P_2-stage:	
H_2O_2, %	1.0
NaOH, %	1.5
$MgSO_4$, %	0.2
DTPA, %	0.2
Consistency, %	10
Temperature, ^{0}C	70
Time, min	180
pH, begin/end	11.2/11.0
Rest of peroxide, %	0.6
Results:	
End brightness, %	84.3
Brightness loss, %	3.38
Limiting viscosity No, mL/g	486

Table V. TCF sequence including ozone stage (high consistency) - OAZ_hP

Oxygen stage: Described in Table II.				
Acidification stage:				
Consistency, %		10		
Temperature, ^0C		60		
Time, min		60		
Acidification with H_2SO_4 to pH		2		
Actual pH, final		2		
Z-stages:	Z1	Z2	Z3	Z4
Consistency, %	40	40	40	40
Temperature, ^0C	40	40	40	40
Time, min	1.5	3.0	4.5	6.0
Brightness, %	68.9	74.9	77.1	78.9
P-stage (equal for all Z-variants):				
H_2O_2, %		3.0		
NaOH, %		1.5		
$MgSO_4$, %		0.2		
DTPA, %		0.2		
Consistency, %		10		
Temperature, ^0C		70		
Time, min		180		
pH, begin/end		10.6/10.7		
Rest of peroxide, %		1.1		
Results:	OAZ_1P	OAZ_2P	OAZ_3P	OAZ_4P
End brightness, %	88.4	90.4	90.6	91.4
Brightness loss, %	1.56	1.50	1.07	1.55
Lim.viscosity No, mL/g	476	445	423	412

Table VI. TCF sequence including ozone stage (high consistency), without oxygen – AZ_hP

Acidification stage:				
Consistency, %		10		
Temperature, ^0C		60		
Time, min		60		
Acidification with H_2SO_4 to pH		2		
Actual pH, begin/end		2		
Z-stages:	Z1	Z2	Z3	Z4
Consistency, %	40	40	40	40
Temperature, ^0C	40	40	40	40
Time, min	1.5	3.0	4.5	6.0
Brightness, %	58.4	61.4	63.6	66.6
P-stages(equal for all Z-variants):				
H_2O_2, %		3.0		
NaOH, %		1.5		
$MgSO_4$, %		0.2		
DTPA, %		0.2		
Consistency, %		10		
Temperature, ^0C		70		
Time, min		180		
pH, begin/end		10.6/10.7		
Rest of peroxide, %		round 1.1 (increases with time used in the Z stage)		
Results:	AZ_1P	AZ_2P	AZ_3P	AZ_4P
End brightness, %	86.3	87.0	88.9	89.1
Brightness loss, %	1.46	1.46	1.69	1.61
Lim.viscosity No, mL/g	445	439	422	437

Table VII. TCF sequence including ozone stage (low consistency), with oxygen – OAZ_1P

Acidification stage:			
Consistency, %		10	
Temperature, ^0C		60	
Time, min		60	
Acidification with H_2SO_4 to pH		2	
Actual pH, begin/end		2	
Z-stages:	Z1	Z2	Z3
Consistency, %	10	10	10
Temperature, ^0C	40	40	40
Time, min	3.5	5.0	8.0
Brightness, %	61.1	62.7	63.6
P-stage(equal for all Z-variants):			
H_2O_2, %		3.0	
NaOH, %		1.5	
$MgSO_4$, %		0.2	
DTPA, %		0.2	
Consistency, %		10	
Temperature, ^0C		70	
Time, min		180	
pH, begin/end		10.9/11.4	
Rest of peroxide, %		round 0.25	
Results:	OAZ_1P	OAZ_2P	OAZ_3P
End brightness, %	85.5	85.1	86.4
Brightness loss, %	2.86	2.27	2.70
Lim.viscosity No, mL/g	493	487	467

7. Comments (1)

The results of brightness and limiting viscosity number show that the oxygen stage is obviously very favourable to both ECF and TCF bleaching sequences. It does not cause any strong deterioration of the cellulose molecule (viscosity). At the same time, chlorine chemicals can be reduced to a certain level.

It is possible to reach target brightness with **ECF** sequences: with oxygen, ODED (total active Cl= 3,5 %) or without oxygen, **DEpD** (total active Cl= 3.5 % and 0.5 % of peroxide for extraction stage).

In the case of TCF sequences, it is easier to achieve target brightness if we have oxygen and ozone in the sequence. Thus, better viscosity values are reached as well.
The important parameter is consistency of the ozone stage. The fear of loosing too much strength with a high-consistency ozone stage has not confirmed. It looks like the high consistency (close to 40 %) offers enough thick water surface layer to protect the fibres from destruction. On the other hand, the reaction time during high consistency is short enough and keeps the inside of the fibres more or less intact.

The proposed **TCF** sequence is **OAZ_hP** (with high consistency ozone stage and with peroxide 3 %, event. with decreased amount, due to it's high residue).

The amount of ozone needed for bleaching was measured during the large scale experiments (further on described).

8. Selected ECF and TCF bleaching sequences in order to prepare enough pulp for testing and sample sheets preparation

Larger quantity of sisal pulp (delivered by UNIDO) was bleached according to the bleaching conditions selected for ECF and TCF bleaching sequences (described in Chapter 6.2) in order to have enough pulp for testing and preparing the required amount of sample sheets. The trials were conducted in a stainless steel vessel rotating in the electrical heated comora. The capacity of the vessel was 1 kg of o.d.pulp.
The detailed bleaching conditions for ECF sequence (DEpD) and for TCF sequence (OAZP) are presented in the next two tables.

Table VIII. Conditions for large scale ECF bleaching trial: DEpD

Trial	DEpD
D_1-stage:	
ClO_2, as act.Cl added, %	2.0
pH, begin/end	2.2/3.3
Consistency, %	10
Reaction time, min	60
Temperature, C	50
Rest of Cl, %	0.05
Ep*-stage:	
NaOH, %	1.0
H_2O_2, %	0.5
Rest of H_2O_2, %	0.1
pH, begin/end	11.3/11.1
Consistency, %	10
Temperature, C	50
Reaction time, min	90
D_2-stage:	
ClO_2, as act.Cl added, %	1.5
pH, begin/end	3.6/3.8
Consistency, %	10
Temperature, C	60
Time, min	180
Rest of Cl, %	0.05

Table IX. Conditions for large scale TCF bleaching trial: OAZP

Oxygen stage:	
Described in Table II.	
Acidification stage:	
Consistency, %	10
Temperature, ^{0}C	60
Time, min	60
Acidification with H_2SO_4 to pH	2
Actual pH, final	2
Z-stage:	
Consistency, %	40
Temperature, ^{0}C	40
Ozone - charged, % (calculated on o.d.pulp)	1.96
Ozone - consumed, %	1.10
P-stage:	
H_2O_2, %	2.0
NaOH, %	1.5
$MgSO_4$, %	0.2
DTPA, %	0.2
Consistency, %	10
Temperature, ^{0}C	70
Time, min	180
pH, begin/end	10.6/10.7
Rest of peroxide, %	0.77

At the end of each sequence the pulp was washed with SO_2-water to 4.5 pH, at 3 % consistency and for 15 min.
Sample sheets were made of both bleached pulp grades according to the standard method for testing and presentation of the "project-work".
Physical properties of both, ECF and TCF bleached grades are shown in Table X.

Table X. Characterization of unbleached, selected ECF and TCF bleached pulps (pulp, delivered by UNIDO)

Property	Unbleached				DEpD				OAZP			
Kappa No.	9.2											
Brightness ISO	38.7				88.8				90.0			
Viscosity SCAN	572				458				432			
Final pH	9.5				7.7				7.9			
Dirt counting (mm^2/m^2)	35.8				30.8				35.8			
Fiber length w.w.av. (mm)	2.06				1.87				1.97			
Fiber width (μm)	ca. 25				ca. 25				ca. 25			
Coarsness (mg/m)	0.125				0.186				0.182			
Opacity (%)	96.0				73.8				71.8			
PFI beating:												
No. of revolutions*	Ø	3000	4000	5000	Ø	3000	4000	5000	Ø	2000	3000	4000
Beating degree (SR)	13	22	32	56	14	21	35	52	14	19	32	48
Freeness (CSF)	770	550	400	175	770	560	360	210	770	600	400	225
Basis weight (g/m^2)	62.2	63.9	63.4	65.2	66.1	60.3	63.3	62.7	60.1	64.9	64.3	64.3
Density (kg/m^3)	300	540	570	630	290	520	590	630	290	530	570	620
Tensile index (N.m/g)	6.0	38.5	42.5	48.0	5.5	35.0	42.0	45.5	5.5	31.5	37.0	39.0
Breaking length (km)	0.61	3.93	4.35	4.93	0.56	3,55	4.30	4.63	0.59	3.20	3.78	3.95
Tear index ($mN.m^2/g$)	2.19	8.26	7,.24	6.21	2.27	8.05	6.86	5.79	2.51	7.44	6.26	5.04
Burst index ($kPa.m^2/g$)	0.56	3.12	7.92	4.15	0.59	3.17	3.58	3.66	0.63	2.51	3.01	3.18
Porosity (μm/Pa.s)	**	190	78	12	**	195	52	16	**	250	93	24

* No. of revolutions at PFI beater
** Too high porosity of being measured

9. Selected ECF and TCF bleaching sequences for sisal pulp, delignified at the Institute in order to determine the physical properties

A defined quantity of sisal fibres (delivered by UNIDO) was delignified according to the suggested pulping conditions (Chapter 5) and bleached according to selected ECF and TCF bleaching sequences (Chapter 8, Tables VIII and IX) in order to test the pulp prepared in a laboratory scale. The Physical properties of both pulp grades are presented in Table XI.

Table XI. Characterization of unbleached, selected ECF and TCF bleached pulps (fibres pulped at the Institute)

Property	Unbleached				DEpD				OAZP			
Kappa No.	12.1											
Brightness ISO	34.7				89.0				91.6			
Viscosity SCAN	969				878				676			
Final pH	8.7				7.5				8.1			
Dirt counting (mm^2/m^2)	139				26.2				25.0			
Fiber length w.w.av. (mm)	2.29				2.23				2.06			
Fiber width (μm)	ca. 25				ca. 25				ca. 25			
Coarsness (mg/m)	0.144				0.124				0.125			
Opacity (%)	97.6				73.4				72.8			
PFI beating:												
No. of revolutions*	Ø	4000	5000	6000	Ø	4000	6000	8000	Ø	4000	5000	6000
Beating degree (SR)	11	25	38	47	12	22	34	50	13	25	34	47
Freeness (CSF)	>800	480	320	280	>800	550	370	210	800	480	370	250
Basis weight (g/m^2)	62.4	62.6	65.0	64.5	63.5	64.7	64.4	64.3	64.6	64.4	65.0	64.0
Density (kg/m^3)	330	600	630	670	320	610	660	710	350	610	670	680
Tensile index (N.m/g)	14.5	86.0	91.5	94.0	12.5	72.5	87.0	93.5	14.0	73.5	80.0	77.0
Breaking length (km)	1.50	8.76	9.35	9.57	1.29	7.39	8.84	9.54	1.44	7.51	8.13	7.85
Tear index ($mN.m^2/g$)	5.96	16.4	14.5	13.2	6.01	18.2	15.3	13.1	6.07	14.6	13.2	13.0
Burst index ($kPa.m^2/g$)	0.85	7.70	8.71	8.88	0.86	6.88	8.28	8.84	0.93	6.48	6.99	7.78
Porosity (μm/Pa.s)	**	44	12	4.4	**	92	8.9	1.6	**	45	10	3.6

* No. of revolutions at PFI beater
** Too high porosity of being measured

10. Comments (2)

The main scope of this work was to select ECF and TCF bleaching sequences of sisal pulp which enable the pulp to reach the brightness level of 88 % ISO. This aim was achieved in both cases, with sisal pulp delivered by UNIDO, and sisal fibres which were pulped and bleached at the Institute.

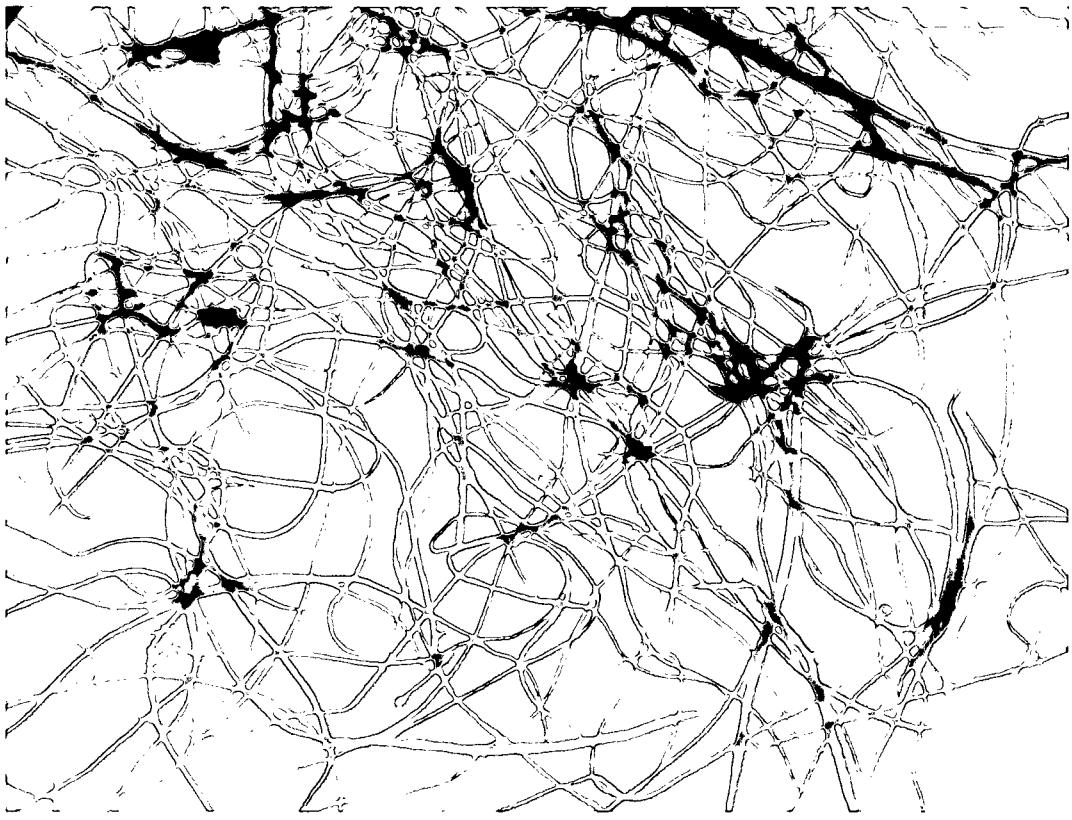
There are quite noticable difference in pulp quality between both bleached pulps. The differences were probably caused by the pulping conditions which were evidently different. That is, the conditions carried out in the plant could not be paralleled with those one in the laboratory. Another reason could be that the pulp delivered by UNIDO was practically oven-dried. Our pulp was de-watered only to ca. 30 % dry matter content. The constant water content obviously has a great influence on fibre quality. It makes hydrogen bonds to loosen more easily after the re-wetting of the fibres. Therefore, the never-dried fibres have always higher mechanical properties than a dried ones. However, this depends on how the drying process is conducted as well.

There were some difficulties in the laboratory sample sheet preparation of unrefined pulp samples.

To conclude, sisal pulp generally has the excellent properties.

Enclosed:
Fibre photomicrographs, optical microscope, magnification 60×, coloration: Graff "C"
Illustration1 unbleached sisal pulp (Unido)
Illustration 2 unbleached sisal pulp (delignified at the Institute)

Ill. 1



Ill. 2