

CHEMICAL AND THERMOGRAVIMETRIC ANALYSIS AND SODA AND ORGANOSOLV PULPING OF *HESPERALOE FUNIFERA*

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The *Hesperaloe funifera* plant was characterized in terms of its major components (cellulose, hemicellulose, lignin and extractives), hot water solubles, 1% NaOH solubles and ash, by using conventional chemical methods and thermogravimetric analysis. The contents in lignin, α -cellulose, holocellulose, hemicellulose, ethanol–benzene extractives, hot water solubles, 1% NaOH solubles and ash of *Hesperaloe funifera* were of 7.3, 40.9, 76.5, 35.6, 4.0, 13.5, 29.5 and 5.9%, respectively. By its chemical composition, *Hesperaloe funifera* provides an effective source of cellulose for producing pulp and paper, with some advantages over other non-wood raw materials including kenaf, bagasse, cotton stalks, wheat straw, paulownia and sunflower stalks. The application of soda and organosolv (ethyleneglycol, diethyleneglycol, ethanolamine and diethanolamine) processes to *Hesperaloe funifera* determined a very good performance of the pulp samples, especially of those obtained by 10% soda and 1% anthraquinone at 155 °C, for 30 min. In fact, the resulting soda–anthraquinone pulp exhibits good yield (48.3%), Kappa number (15.2), viscosity (737 mL/g) and beating degree (65.1 °SR), the paper sheets obtained from it evidencing good tensile index (83.6 Nm/g), stretch (3.8%), burst index (7.34 KN/g) and tear index (3.20 mNm²/g) values.

Keywords: *Hesperaloe funifera*, composition, soda pulping, organosolv pulping, paper

INTRODUCTION

The paper industry currently produces more than five hundred types of paper for over three hundred uses. More than 30% of the paper types used at present (*e.g.* filter, chromatographic, interleaving, electrotechnical paper) did not even exist only ten years ago, having emerged in response to the new social needs.¹ The increasing variety of paper types and uses has resulted in a substantial increase² in production, from 187 million tons in 2000 to 195 millions in 2007 (*i.e.* a 4.3% rise). Over this period, the pulp production from wood species has grown by 3.1%, while the use of non-wood species for such purposes increased much more markedly² (18.1%), which indicates the growing significance of the latter as cellulose raw materials. This phenomenon can be ascribed to the fact that non-wood plants provide an effective alternative to wood, paper and cellulose pulp imports for the developing countries with poor forest resources, and also that agrifood residues

acquire an added value when used for pulping. In fact, the special chemical composition and morphological characteristics of non-wood raw materials (*e.g.* their less compact, more porous structure, more readily accessible tissues and weaker interfibrillar bonds) reduce the energy requirements and reagent consumption during cooking and bleaching processes.

Hesperaloe funifera, belonging to the *Agavaceae* family, is up to 80 cm tall and 1.0–1.2 m wide, with long leaves, up to 5 cm wide and 2–3 cm thick. All species of its genus originated in Mexico and in its neighbouring USA regions, where it is used mainly for ornamental purposes.³

Hesperaloe has very modest irrigation requirements, which is the effect of its utilising the acid metabolism of *Crassulaceans* (CAM) for photosynthesis. Its plants fix the carbon dioxide and transpire water more intensely at night than during the day; also, because of the

lower coefficient of transpiration at night, they use water highly efficiently. Based on these properties, *Hesperaloe* might be an effective cellulose raw material in arid zones, precluding cultivation of other species,^{4,6} or in areas with scarce water resources. The first crop takes five years to develop in full, the plant giving a new crop every three years afterwards. High-density plantations (27000 per hectare) can yield 205 tons of fresh biomass per hectare per crop, which amounts to approximately 20 tons of dry biomass per hectare, crop and year after the initial crop.⁵ These crop yields can be increased by a careful control of plant flowering and by higher planting densities.⁷

Although the fibre morphology of *Hesperaloe funifera* is especially suitable for making cellulose pulp,⁸ the researches initiated in this direction are scarce. With a few exceptions, the material was subjected to alkaline sulphite–anthraquinone or soda–anthraquinone pulping,^{5,9,10} and the resulting paper sheets evidenced very high tensile, burst and tear indices – which makes them highly suitable for special papers.

In this work, *Hesperaloe funifera* was characterized physico-chemically, then subjected to soda and organosolv processes for obtaining paper pulp.

Some authors have used alternative methods to conventional chemical analysis, to characterize the lignocellulosic materials. Such alternatives include high-pressure liquid chromatography (HPLC),¹¹ near infrared spectroscopy (NIRS)¹² and also, occasionally, thermogravimetric analysis (TGA).¹³⁻¹⁵

Soda and soda–anthraquinone processes have been used to pulp non-wood raw materials¹⁶⁻¹⁹ with good results, if considering the advantages they provide, such as:

- (a) high throughput resulting from the use of relatively short pulping times
- (b) good yields
- (c) applicability to both wood and non-wood raw materials
- (d) reusability of cooking liquors
- (e) increased yields, more expeditious cooking and reduced Kappa numbers resulting from the joint use of soda and anthraquinone.

Organosolv processes have been widely used at a laboratory scale,^{20,21} being applied to various alternative raw materials including *Cynara cardunculus*, wheat straw, *Paulownia fortunei*, vine shoots, cotton stalks, *Leucaena leucocephala* and *Chamaecytisus proliferus*.²²⁻

²⁵ The most salient advantages of these processes are:

- (a) economy at a small or medium scale, efficient recovery of solvents and by-products, as compared to kraft processes
- (b) reduced water, energy and reagent consumption
- (c) reduced pollution and easy recovery of pulping effluents
- (d) applicability to wood and non-wood raw materials
- (e) production of pulp with properties similar to those of kraft pulp, in addition to higher yields, lower lignin contents, higher brightness and easier bleaching and refining
- (f) no need for additional investments if kraft pulping facilities are available, as the application of high-boiling solvents (glycols, ethanalamines) is sufficient to exploit them.

In the present work, *Hesperaloe funifera* was characterized in terms of its major components (cellulose, hemicellulose, lignin and extractives), and also of hot water solubles, 1% NaOH solubles and ash, by using conventional chemical methods, in addition to thermogravimetric analysis of its major components. In a subsequent stage, the *Hesperaloe funifera* samples were subjected to soda, soda–anthraquinone, ethyleneglycol, diethyleneglycol, ethanalamine and diethanalamine pulping, and the resulting pulp and paper sheets were analyzed as to the usual quality-related parameters.

EXPERIMENTAL

Characterization of *Hesperaloe funifera*

The samples of *Hesperaloe funifera* fibre were kindly supplied by the Hesperaloe Project research team from the University of Arizona for educational and research purposes. After drying at room temperature, the raw material was cold-ground in a Retsch SM 2000 mill, to avoid alterations of its components. The ground product was sieved and the 0.25-0.40 mm fraction (sieves No. 60 and 40 in the Tyler series) was saved for analysis (particles larger than 0.40 mm are inefficiently attacked by chemical reagents, while those smaller than 0.25 mm can interfere with the filtering operations).

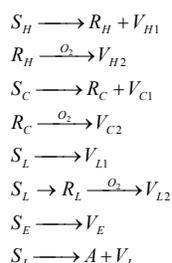
Chemical analysis

The lignin, α -cellulose, ethanol–benzene extractives, hot water solubles, 1% NaOH solubles and ash contents of the raw material were determined in accordance with the following Tappi standards: T-222, T-203 0S-61, T-204, T-257, T-212 and T-211. The content of holocellulose was assessed by Wise's method.²⁶

Thermogravimetric analysis

Thermogravimetric runs were performed on a Mettler Toledo TGA/SDTA851e/LF1600 instrument, using *ca.* 5 mg of sample. Combustion runs, carried out in synthetic air (N₂/O₂ 4:1), involved heating from 25 to 900 °C at a rate of 5, 10 or 20 °C/min.

The combustion process was modelled¹⁵ in accordance with Scheme 1, where S_i represents the initial solid fractions of each component, R_i – the solid residues obtained from their volatilization, V_i – the yielded volatiles, A – the ash produced by inorganic materials, and subscripts H, C, L, E and I denote hemicellulose, cellulose, lignin, extractives and inorganic compounds, respectively.



The experimental data were simulated by the autocatalytic kinetic equation¹⁵:

$$\frac{dV_i}{dt} = k_i V_{\infty i} \left(1 - \frac{V_i}{V_{\infty i}}\right)^{n_i} \left[s + \left(\frac{V_i}{V_{\infty i}}\right)^m\right] \quad (1)$$

where k_i is the kinetic constant (dependent on the pre-exponential factor, k_0 , and activation energy, E), n – the reaction order, m – the nucleation order, s is a factor equal to 0.01 and $V_{\infty i}$ – the mass of volatiles at infinite time.

The thermogravimetric data for *Hesperaloe* combustion, as the final reference, were used to integrate the kinetic equations by the Runge-Kutta method optimized with the Gauss-Newton method, for obtaining a minimum in the following objective function:

$$OF = \sum_{i=1}^n \left(\frac{dm_{exp}}{dt} - \frac{dm_{cal}}{dt} \right)^2 \quad (2)$$

where dm_{exp}/dt and dm_{cal}/dt are the experimental and calculated mass loss rates, respectively, for the n points of each experiment.

Fibre length

Fibre length distribution of *Hesperaloe funifera* was determined on a Visopan projection microscope, after micro-cooking the raw material with 10% soda at 80 °C, for 1 h, and subsequently staining the fibres with 1% safranin.

Pulping

The raw material was cooked in a 15 L batch reactor heated with an outer jacket and stirred by rotating the vessel *via* a motor connected through a rotary axle to a control unit including the required instruments for measurement and control of pressure and temperature.

Table 1 lists the values of temperature, time and concentrations of the reagent (soda, anthraquinone) or solvent (ethyleneglycol, diethyleneglycol, ethanolamine, diethanolamine) used in the pulping experiments. According to literature data, the liquid/solid ratio was always 8:1. When each process was completed, the cooked material was unloaded from the reactor, washed to remove the residual cooking liquor and fiberized in a disintegrator at 1200 rpm for 30 min, which was followed by beating in a Sprout-Bauer refiner. Finally, the fiberized material was passed through a 0.16 mm pore size filter, to remove the uncooked particles.

Characterization of pulp and paper sheets

The pulp samples obtained were characterized in terms of yield (gravimetrically), and also for Kappa number, viscosity and beating degree – in a Shopper-Riegler apparatus – according to the UNE standards 57-034, 57-039 and 57-025, respectively.

Paper sheets were obtained with an Enjo-F39-71 former and analysed for tensile index, stretch, burst index, tear index and brightness, in accordance with the following UNE standards: 57-054, 57-028, 57-08, 57-033 and 57-062.

RESULTS AND DISCUSSION

Physico-chemical properties

The contents in lignin, α -cellulose, holocellulose, hemicellulose, ethanol–benzene extractives, hot water solubles, 1% NaOH solubles and ash of *Hesperaloe funifera* were of 7.3, 40.9, 76.5, 35.6, 4.0, 13.5, 29.5 and 5.9%, respectively. Figure 1 compares the holocellulose, α -cellulose and lignin contents of this species with those of other non-wood materials.^{23,25,27-31} As one can see, *Hesperaloe funifera* has the lowest proportion of lignin and an α -cellulose content similar to that of other raw materials, except EFB and cotton stalks, which surpass it in this respect. A low hemicellulose content can raise the necessary energy to obtain a given tensile strength level of conifer pulp.³²

Figure 2 shows the thermogravimetric curve (TG) and its derivative (DTG) for the studied raw material. As seen, the curve exhibits two steps of mass loss, due to volatilization and char oxidation, respectively. Minimizing the differences between the TG data and those obtained by optimizing the combustion model of Scheme 1 for each *Hesperaloe* component allowed us to compile two sets (volatilization and char oxidation), which contained the pre-exponential factor (k_0), activation energy (E), reaction order (n), nucleation order (m) and mass of volatiles at infinite time ($V_{0\infty}$). Table 2 shows the average

values of the kinetic parameters obtained at the three heating rates studied, and Figure 3 compares the experimental and simulated DTG curves. The volatilization and char oxidation zones for each component are shown. A good

agreement with the experimental results was noticed.

The composition of each sample was determined by adding up the masses of volatiles obtained in both steps.

Table 1
Pulping conditions of *Hesperaloe funifera* pulp obtained with soda, soda-AQ, ethanolamine, diethanolamine, ethyleneglycol and diethyleneglycol

Pulp	Reactive	Temperature, °C	Time, min	Concentration, % (o.d.r.m.)
P1	Soda*	155	30	10
P2	Soda*	170	60	15
P3	Soda*	185	90	20
P4	Soda	155	30	10
P5	Soda	170	60	15
P6	Soda	185	90	20
P7	Ethanolamine	160	30	60
P8	Ethanolamine	170	60	70
P9	Ethanolamine	180	90	80
P10	Diethanolamine	160	30	60
P11	Diethanolamine	170	60	70
P12	Diethanolamine	180	90	80
P13	Ethyleneglycol	160	30	60
P14	Ethyleneglycol	170	60	70
P15	Ethyleneglycol	180	90	80
P16	Diethyleneglycol	160	30	60
P17	Diethyleneglycol	170	60	70
P18	Diethyleneglycol	180	90	80

*1% anthraquinone

According to Table 2, the hemicellulose in *Hesperaloe* accounts for 33.8 wt% (26.6 + 6.2), cellulose – for 40.4 wt% (27.7 + 12.27), lignin – for 12.0 wt% (8.7 + 3.3), the extractive fraction – for 3.9 wt% (2.2 + 1.7) and the inorganic materials – for 2.5 wt%. These results are consistent with those of chemical analysis. Some difference in the lignin content is always inevitable: the lignin fraction considered in the corresponding Tappi standard consists solely of insoluble lignin, whereas TG analyses detect all lignin present. Table 3 shows the results of *Hesperaloe funifera* characterization by conventional methods and thermogravimetric analysis.

Figure 4 shows the fibre length distribution curve for *Hesperaloe funifera* and a

photograph of a fibre sample. The mean fibre length, of 4.19 mm, exceeds that of some non-wood pulping raw materials, such as kenaf (1.3 mm), reed (1.2 mm), switchgrass (1.1 mm), miscanthus (1.0 mm), cotton stalks (0.8 mm) and wheat straw (0.7 mm).³³ Fibre length and thickness are correlated with several mechanical properties of paper. Thus, the long fibres have a favourable effect on the tensile index and tear index; also, thin-walled and low in diameter fibres result in increased paper strength, bonding and in easy sheet formation.³³ The long fibres of *Hesperaloe funifera* are extremely strong and possess a low linear mass, which ensures the obtainment of paper with good surface properties.

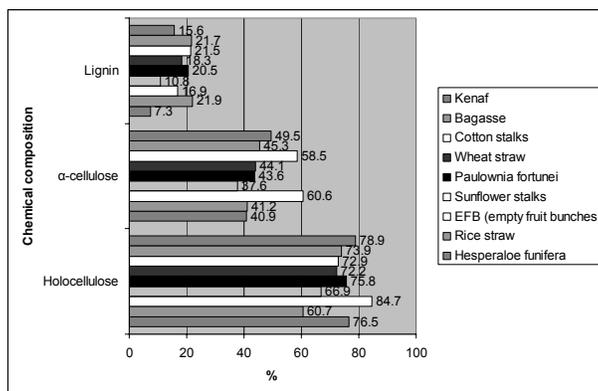


Figure 1: Chemical composition of *Hesperaloe funifera* and other raw materials

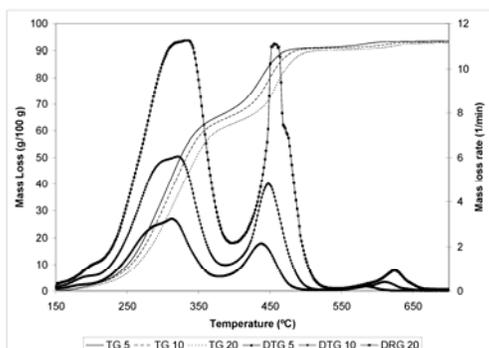


Figure 2: TG and DTG curves of *Hesperaloe funifera* at different heating rates

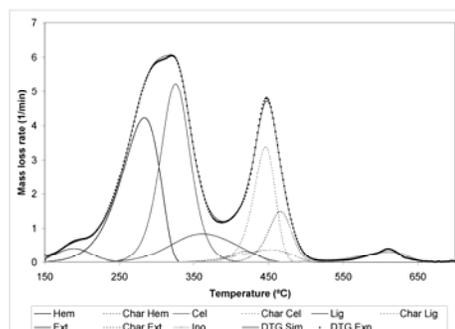


Figure 3: Simulation of *Hesperaloe funifera* combustion. Heating rate of 10 °C/min

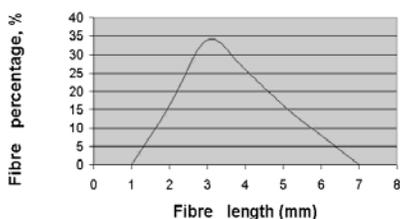


Figure 4: Graph of *Hesperaloe funifera* fibre size distribution and fibre photograph



Pulp

Figure 5 shows the results of the characterization of *Hesperaloe funifera* soda and soda-anthraquinone pulp obtained under the conditions summarized in Table 3, in terms of yield, Kappa number, viscosity and beating degree. The well-known pulping action of anthraquinone involves redox catalysis of some reactions occurring during cooking of the raw material.^{34,35} The electrons in the aldehyde groups of the carbohydrate present in its fibres are transferred to the anthraquinone molecule and, consequently, the aldehyde groups are transformed into carboxyl groups, which stabilizes the carbohydrates and increases pulp yield.³⁶ Our soda-anthraquinone pulp samples (P1-P3) exhibited better yield, Kappa number and viscosity than those obtained in the absence of a catalyst.

Thus, the *Hesperaloe* pulp obtained by cooking with 10% NaOH and 1% anthraquinone at 155 °C for 30 min (P1) exhibited the highest yield (48.3%) and viscosity (737 mL/g) values, in addition to a fairly low Kappa number (15.2).

Figure 6 shows the results of the characterization of *Hesperaloe funifera* pulp obtained by using various organosolv reagents (ethanolamine, diethanolamine, ethyleneglycol and diethyleneglycol) under the conditions stated in Table 1. The pulp samples obtained with amine solvents (P7-P12) exhibited better yield, Kappa number, viscosity and beating degree than those provided by glycols. The highest yield (59.6%) was recorded for the pulp obtained at 60% ethyleneglycol concentration, at 160 °C for 30 min (P13); diethanolamine provided pulp with a similar

yield, but significantly better values for the other properties. Thus, the best Kappa number (20.1) was obtained by pulping with 70% diethanolamine at 170 °C for 60 min (P11), or at 80% amine concentration, at 180 °C for 90 min. Apparently, the reaction conditions have little influence on the Kappa number, which allows obtaining of *Hesperaloe* pulp with comparable Kappa number, at lower

temperature, time and solvent concentration – and hence with reduced production costs. This is also the case of viscosity, which peaked in the pulp samples obtained with diethanolamine (P10-P12); there was a difference of only 26 mL/g between the level reached under the most drastic conditions and that reached under the least drastic ones: 814 mL/g for P11 vs 788 mL/g for P10.

Table 2
Kinetic parameters for *Hesperaloe* combustion

	Component	$\text{Ln } k_o \text{ (s}^{-1}\text{)}$	$E \text{ (kJmol}^{-1}\text{)}$	n	m	$V_\infty \text{ (%)}$
Volatilization	Hemicellulose	14.3 ± 0.1	90 ± 1	0.87 ± 0.03	0.01 ± 0.01	27.6 ± 0.2
	Cellulose	35.2 ± 0.1	198 ± 1	1.75 ± 0.05	0.01 ± 0.01	27.7 ± 0.4
	Lignin	6.8 ± 0.1	65 ± 1	2.96 ± 0.01	0.39 ± 0.03	8.7 ± 1.5
	Extractable	13.4 ± 0.1	71 ± 2	1.36 ± 0.02	0.11 ± 0.02	2.2 ± 0.2
	Inorganic	20.8 ± 0.1	191 ± 2	0.86 ± 0.05	0.30 ± 0.02	2.5 ± 0.1
Char oxidation	Hemicellulose	19.55	146 ± 3	1.12 ± 0.02	0.7 ± 0.1	6.2 ± 0.1
	Cellulose	19.55	142 ± 4	0.97 ± 0.01	0.6 ± 0.2	12.7 ± 0.1
	Lignin	19.55	150 ± 2	1.08 ± 0.02	0.01 ± 0.01	3.3 ± 0.6
	Extractable	19.55	140 ± 1	0.94 ± 0.01	0.32 ± 0.01	1.7 ± 0.1

Table 3
Results of *Hesperaloe funifera* characterization
by conventional methods and thermogravimetric analysis

Component	Method of analysis	
	TAPPI	Thermogravimetric
Hemicellulose (%)	35.6	33.8
α -cellulose (%)	40.9	40.4
Holocellulose (%)	74.2	76.5
Ethanol-benzene extractibles (%)	4.0	3.9

Paper sheets

Table 4 shows the results of the characterization of paper sheets obtained from the previous *Hesperaloe* pulp samples. As seen, the sheets made from soda pulp possess better physical properties than those obtained from soda-anthraquinone pulp. The best tensile index, stretch, burst index and tear index were obtained under the mildest conditions used (P4), *i.e.* with the least reagent and heating energy consumption.

The physical properties of the paper obtained from the amine pulp samples were better than those of the paper made from glycol pulp samples. The best tensile index was achieved with 60% ethanolamine, at 160 °C for 30 min. Also, the highest brightness,

stretch, burst index and tear index were obtained with ethanolamine, both under mild and drastic operating conditions.

Comparison with other raw materials

Table 5 shows the results of the characterization of pulp and paper sheets obtained from other raw materials.^{18,30,36-38} As can be remarked, Abaca surpasses *Hesperaloe* in yield, viscosity, stretch and tear index. Oil palm surpasses *Hesperaloe* in tear index and viscosity, while the opposite is true for the other pulp and paper properties. Sugarcane bagasse provides a better yield and tear index than those of *Hesperaloe*. Finally, rice straw and kenaf are similar to *Hesperaloe* in yield, but provide a worse tear index and better values for the other studied properties.

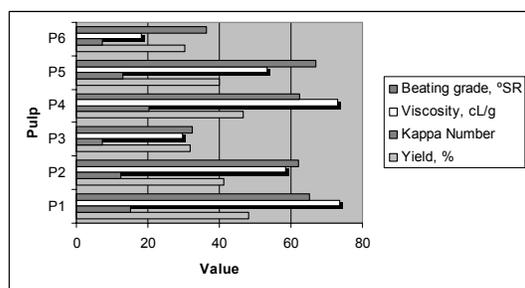


Figure 5: Properties of *Hesperaloe funifera* pulp obtained with soda and soda-AQ

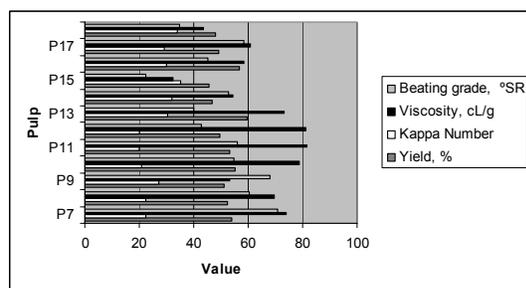


Figure 6: Properties of *Hesperaloe funifera* pulp obtained with ethanolamine, diethanolamine, ethyleneglycol and diethyleneglycol

Table 4
Properties of paper sheets made from *Hesperaloe funifera* pulp obtained with various reagents

Pulp	Reagent	Tensile index, Nm/g	Stretch, %	Burst index, KN/g	Tear index, mNm ² /g
P1	Soda*	83.6	3.8	7.34	3.20
P2	Soda*	70.7	4.0	5.34	3.22
P3	Soda*	23.8	2.2	1.09	1.00
P4	Soda	83.8	4.4	6.93	3.47
P5	Soda	68.4	4.4	5.28	3.48
P6	Soda	34.3	2.7	2.59	1.29
P7	Ethanolamine	81.6	3.0	5.41	2.09
P8	Ethanolamine	64.3	2.7	5.33	3.11
P9	Ethanolamine	59.8	3.6	4.81	3.45
P10	Diethanolamine	79.0	3.0	6.82	3.01
P11	Diethanolamine	73.9	3.3	5.55	3.00
P12	Diethanolamine	63.8	3.7	5.62	5.22
P13	Ethyleneglycol	74.5	2.6	6.09	2.92
P14	Ethyleneglycol	43.4	3.5	0.38	4.37
P15	Ethyleneglycol	13.8	1.6	3.96	0.95
P16	Diethyleneglycol	79.5	2.8	5.82	2.67
P17	Diethyleneglycol	47.6	3.3	3.55	2.51
P18	Diethyleneglycol	18.3	1.8	0.45	0.91

* with addition of 1% anthraquinone

Table 5
Properties of pulps and paper sheets obtained using different reagents of various raw materials

Parameter	Abaca	<i>Phoenix dactilifera</i> soda	<i>Phoenix dactilifer</i> soda-AQ	Bagasse	Rice straw organosolv	Kenaf
Yield, %	90.7	42.1	44.2	82.7	35.6-53	58.1
Kappa number	10.6	28.9	25.5	92.9	17.0-75.3	25.5
Viscosity, mL/g	1428	814	937	-	673-956	-
Tensile index, Nm/g	55.9	37.3	43.1	62.9	21.1-23.7	11.4
Stretch, %	5.12	-	-	-	1.95-1.99	0.68
Burst index, KN/g	-	1.9	2.2	2.8	1.0-1.2	2.4
Tear index, mNm ² /g	19.03	10.7	10.0	6.0	0.3-0.4	11.8

CONCLUSIONS

A comparison between the chemical properties of *Hesperaloe funifera* and those for other non-wood pulping raw materials,

including kenaf, bagasse, cotton stalks, wheat straw, paulownia, sunflower stalks, EFB and rice straw, revealed that the former is an effective alternative source of cellulose fibre

for pulp and paper production.

Analytically, the thermogravimetric technique was found useful in determining the composition of the biomass samples. The TGA results obtained in atmospheric air were in fact consistent with those provided by conventional chemical analyses.

Based on the results of the characterization of pulp and paper obtained by cooking *Hesperaloe funifera* with soda, soda-anthraquinone, ethyleneglycol, diethyleneglycol, ethanolamine and diethanolamine, the best properties are provided when using 10% soda-1% anthraquinone, at 155 °C for 30 min; these conditions lead to good yield, Kappa number, viscosity, beating degree, tensile index, stretch, burst index and tear index values.

In summary, *Hesperaloe funifera* is a viable alternative raw material for papermaking purposes, on account of its very modest irrigation requirements due to its highly efficient water usage. This makes it an effective choice for obtaining pulp and paper with more than acceptable properties in areas with an arid climate or scant water resources.

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